A COURSE
OF
PRACTICAL CHEMISTRY
FOR
AGRICULTURAL STUDENTS

VOLUME I

BY

L. F. NEWMAN, M.A., F.I.C.

FELLOW OF ST CATHARINE'S COLLEGE, CAMBRIDGE

AND

H. A. D. NEVILLE, M.A., B.Sc., F.I.C.

PROFESSOR OF AGRICULTURAL CHEMISTRY,
UNIVERSITY COLLEGE, READING

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PREFACE

THE following exercises in Practical Agricultural Chemistry are designed primarily for the use of students taking the course for the Degree in Agricultural Science at Cambridge University. Volume I is intended to cover the first year's course on the Chemistry and Physics of the Soil, while Volume II covers the second year's course on the Chemistry of Foods. The latter volume is divided into two parts: Part I dealing with such exercises in Pure Organic Chemistry as are essential for agricultural students, and is entirely qualitative, while Part II deals with quantitative estimations and technical analyses of food stuffs. This division has been considered desirable, as students who have already taken a course in Organic Chemistry will find it unnecessary to work through Part I of Volume II. Volume III deals with the special advanced Chemistry of Insecticides and Fungicides, Food preservatives, etc. It is hoped that this division into convenient booklets will make them useful to teachers. The exercises are designed to illustrate most of the essential points in Agricultural Chemistry and to require the minimum of apparatus.

A Course of Practical Work was compiled by Professor T. B. Wood some years ago for the use of his classes, and this forms the foundation of a portion of the present exercises. The sincere thanks of the authors are due to Professor Wood and the Syndics of the University Press for their permission to utilise that material.

In addition to the directions for practical work, a series of notes has been added to each day's work to explain just those points which considerable experience in teaching in a laboratory has shown to be those on which the student usually needs assistance from the demonstrator to explain the reason and reactions of the experiments as they are being carried out.

It is fully recognised that many of the experiments and accompanying notes could have been elaborated with advantage, but the necessity of restricting apparatus to the limits which it is possible to supply for the use of large classes, and the fact that the notes are only intended as laboratory guides, and not to supersede lectures, have determined the present scope of the volumes.

L. F. N.
H. A. D. N.

December, 1919.

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I

THE AIR

1. Burn a small bit of phosphorus in a bell jar standing in a dish of water and observe the following points:

(*a*) The phosphorus burns very brightly at first, then more feebly and finally goes out.

(*b*) As the phosphorus burns, white fumes are formed which gradually disappear.

(*c*) As the bell jar cools the gas inside decreases considerably in volume. (See note *a*.)

2. Prepare some oxygen by gently heating in a round-bottomed flask, fitted with a delivery tube, a small quantity of a mixture of potassium chlorate and manganese dioxide. (See note *b*.) Collect over water three cylinders of the oxygen which is given off. Place the end of the delivery tube under the bell jar in which the phosphorus was burned and pass in enough oxygen to make up the original volume.

(*a*) Into one of the cylinders of oxygen plunge a splinter of wood which has a glowing spark at the end. The wood at once bursts into flame. This is a common test for oxygen.

(*b*) Burn a bit of phosphorus in the second cylinder and note the great brightness with which it burns.

(*c*) Repeat with the third cylinder using charcoal instead of phosphorus.

(*d*) Burn another piece of phosphorus in the bell jar of nitrogen to which oxygen has been added and note that it burns just as it did in the original air. (See note *c*.)

3. Take a long tube, sealed at one end and fitted with a good rubber bung at the other end. Mark off this tube into five equal parts with either rubber rings or thin strips of gummed label. Remove the bung and introduce into the tube a piece of phosphorus about the size of a pea. Replace the bung. Ignite the phosphorus in the sealed end of the tube by *gently* warming in the bunsen flame. By tilting, run the burning phosphorus down the whole length of the tube. When the phosphorus ceases to burn, place the corked end of the tube under water and remove the cork. Water will pass up into the tube and when the gases have thoroughly cooled, will stand in the tube up to the level of the first division. (See notes *d* and *e*.)

4. Fit a test-tube with a cork and leading tube and arrange for collecting gas over water as in Expt. 2. Introduce into the tube a small quantity of mercuric oxide and heat strongly. Collect a test-tube of the gas evolved (allowing the first bubbles, which are mainly air, to escape) and test with a glowing splinter as in Expt. 2. The gas is oxygen. Notice at the same time that small globules of mercury collect on the cooler parts of the walls of the test-tube.

NOTES

Note a. Air consists of two gases, one of which allows substances to burn in it and is called oxygen, while the other does not allow substances to burn in it and is known as nitrogen. It is the exhaustion of the oxygen by the burning phosphorus which causes the decrease in volume in this experiment, the nitrogen being left. This experiment is an example of what is known as *combustion,* that is the chemical combination of some substance with oxygen to form a new compound. The white fumes observed when phosphorus burns in air consist of phosphorus and oxygen combined to form phosphoric oxide. The fumes disappear because they gradually dissolve in the water.

The combustion of any substance in the presence of oxygen gives an *oxide* or *oxides.*

Note b. The oxygen evolved comes entirely from the potassium chlorate, potassium chloride being left. The manganese dioxide is added because it is found to lower the temperature at which the oxygen is given off from the chlorate. The manganese dioxide is unaltered at the end of the experiment.

In carrying out the experiment care should be taken that the mixture does not block the neck of the flask or the leading tube and that, directly sufficient oxygen has been collected, the delivery tube is removed from the water before the flame is taken away.

Note c. These experiments are examples of the process of combustion as defined in note *a.* In the case of the wooden splinter the chemical elements of the wood, principally *carbon* and *hydrogen,* combine with the oxygen to give an oxide of carbon known as *carbon dioxide* and an oxide of hydrogen known as *water.*

In connection with the process of combustion two points should be noted, first, the reaction results in the production of such a high temperature that the substances become incandescent and, second, that a high temperature is frequently necessary to start the process. In the case of wood, oxidation will not proceed unless a portion of the splinter has been previously heated to incandescence. Similarly when a fire is "lit" in an ordinary grate combustion is started by the high temperature of the burning match but, once started, the heat generated by the oxidation is sufficient to carry the action through the entire mass.

Note d. The tilting of the tube is merely to bring the burning phosphorus into intimate contact with the whole of the enclosed air thereby facilitating the removal of the oxygen.

Note e. The experiment demonstrates that air contains one-fifth of its volume of oxygen.

EQUATIONS

$$4P + 5O_2 = 2P_2O_5$$
Phosphorus + Oxygen = Phosphorus Pentoxide

$$C + O_2 = CO_2$$
Carbon + Oxygen = Carbon Dioxide

$$2KClO_3 = 2KCl + 3O_2$$
Potassium Chlorate = Potassium Chloride + Oxygen

$$2HgO = 2Hg + O_2$$
Mercuric Oxide = Mercury + Oxygen

II

HYDROGEN

1. Prepare hydrogen by adding dilute sulphuric acid to granulated zinc, in a bottle provided with a thistle funnel and delivery tube.

(*a*) Test to see that air is removed from the apparatus, by collecting a test-tube full of gas over water and setting it alight. It will burn quietly as soon as the apparatus is free from air. Then collect three cylinders of hydrogen. (See note *a*.)

(*b*) Invert one cylinder and remove the glass plate. Push a lighted taper up into the gas and note that the gas burns at the mouth of the cylinder but the taper does not burn in the gas. (See note *b*.)

(*c*) Remove the glass plate from a cylinder standing mouth upwards and immediately apply a light. The gas burns away extremely quickly.

(*d*) Repeat (*c*), but wait a few seconds before applying the light. Note that no combustible gas is left in the cylinder. (See note *c*.)

2. Hold a clean cold glass surface over a flame of dry hydrogen burning in air and note that drops of water condense on the surface. (See note *d*.)

3. Show that hydrogen is produced by placing in separate test-tubes small quantities of iron, magnesium and aluminium and adding dilute sulphuric acid to each. The evolution of hydrogen can be demonstrated by proving the gas to be light and inflammable.

4. Repeat, using hydrochloric acid, and note that the gas produced in each case is hydrogen.

5. Repeat, using lead and dilute sulphuric acid. Note that no action takes place. Try the effect of strong nitric acid on zinc and note that the gas evolved is not hydrogen. (See note *e*.)

6. Insert a funnel in a large beaker full of water and place a test-tube also full of water over the stem of the funnel. With a pair of tongs push a small piece of calcium under the funnel and if the action is slow gently warm the beaker over a flame. Note that gas gradually collects in the test-tube. Prove the gas to be hydrogen by testing with a lighted splinter and by burning it. (See note *f*.)

NOTES

Note a. A mixture of hydrogen with oxygen is violently explosive if ignited. The air in the apparatus becomes mixed with the hydrogen first evolved to form an explosive mixture. Therefore the first bubbles passing out of the apparatus should be allowed to escape. In a short time the apparatus will be free from air and hydrogen alone will escape.

Note b. This experiment demonstrates that hydrogen is inflammable but does not support combustion.

Note c. Experiments (c) and (*d*) demonstrate that hydrogen is an exceedingly light gas. Directly the glass plate is removed from the cylinder the hydrogen begins to rise in the surrounding atmosphere, and is replaced in the cylinder by air. Even heavy gases will diffuse into the air in this way but the difference in rates of diffusion between light and heavy gases is most marked.

Note d. When hydrogen burns it combines with oxygen to form water, this substance being an oxide of hydrogen.

Note e. It is to be noted that, as in Experiments 1, 3 and 4, hydrogen is produced by the action of many metals on acids, yet, in some cases, as in Expt. 5, hydrogen is not given off. Where no hydrogen is evolved it may be that no action takes place or that some other gas is produced instead of hydrogen.

Note f. As already stated in note *d*, water is an oxide of hydrogen. The calcium in this experiment unites with the oxygen of the water to produce calcium oxide and liberates hydrogen.

EQUATIONS

$Zn + H_2SO_4 = ZnSO_4 + H_2$
Zinc + Sulphuric Acid = Zinc Sulphate + Hydrogen

$2H_2 + O_2 = 2H_2O$
Hydrogen + Oxygen = Water

$Fe + H_2SO_4 = FeSO_4 + H_2$
Iron + Sulphuric Acid = Iron Sulphate + Hydrogen

$Mg + H_2SO_4 = MgSO_4 + H_2$
Magnesium + Sulphuric Acid = Magnesium Sulphate + Hydrogen

$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2$
Aluminium + Sulphuric Acid = Aluminium Sulphate + Hydrogen

$Fe + 2HCl = FeCl_2 + H_2$
Iron + Hydrochloric Acid = Iron Chloride + Hydrogen

$Mg + 2HCl = MgCl_2 + H_2$
Magnesium + Hydrochloric Acid = Magnesium Chloride + Hydrogen

$2Al + 6HCl = 2AlCl_3 + 3H_2$
Aluminium + Hydrochloric Acid = Aluminium Chloride + Hydrogen

$Ca + H_2O = CaO + H_2$
Calcium + Water = Calcium Oxide + Hydrogen

III

COMPOSITION AND PROPERTIES OF WATER

1. The fact that water is formed by the combination of hydrogen and oxygen has been shown qualitatively in Chapter II. Quantitatively the composition can be shown by the following experiment. Fill the eudiometer tube supplied with water and then, inverting it over water in a trough, collect in it a few bubbles of hydrogen from the hydrogen cylinder. Close the open end of the tube with the thumb and turn the tube so that the gas passes up to the closed end. Remove water from the open end until the water stands at the same level in both limbs. Read and note the volume of hydrogen. Again fill the open end of the tube with water and introduce a few bubbles of oxygen from the oxygen cylinder, transferring the gas as before to the closed end of the tube. Level and note the total volume of gas: Now explode the mixture, holding the thumb on the open end. Level again and read the volume of gas which remains. Transfer the gas to the open end and test with a glowing splinter to find out whether it is oxygen or hydrogen. Calculate the proportions by volume in which the gases have combined. (See note *a*.)

2. Fit up a flask with a two-holed cork, through one hole of which passes a thermometer and through the other a small bent leading tube. The bulb of the thermometer should be about the middle of the neck of the flask while the leading tube should be slipped into a glass tube about two feet long of slightly larger bore. This larger glass tube will act as a condenser and, if inclined at an angle, any liquid condensing in it can be collected at the lower end. Half fill the flask with distilled water and boil. Note that the thermometer rises to a definite temperature and then remains constant during the whole of the experiment. Note this temperature, using in turn both a Centigrade and a Fahrenheit thermometer. Now repeat the experiment, using a strong solution of salt in the flask instead of distilled water. Again note the temperature of the vapour in the neck of the flask but afterwards push down the thermometer until the bulb is in the boiling brine and note whether this is at the same temperature as the vapour. (See note *b*.)

3. Almost fill a beaker of about 500 c.c. capacity with a mixture of ice and salt. Into this freezing mixture place a boiling tube containing 10–20 c.c. water and stand a thermometer in it. Note the temperature of the water at the beginning of the experiment and, while constantly stirring with the thermometer, note the gradual fall in temperature. At a certain temperature it can be felt that ice

crystals are forming in the water and it should be then noted that the temperature remains constant until all the water has become changed to a mass of ice crystals. Note this constant temperature. Take the boiling tube out of the freezing mixture and, again constantly stirring, note that the temperature remains constant so long as any ice crystals are present in the water, after which it rises steadily.

Try the experiment with a strong salt solution in the boiling tube instead of distilled water. (See note *c*.)

4. Evaporate to dryness in three dishes small quantities of (1) sea water, (2) spring water, (3) rain water. Note the relative amounts of solid matter left after evaporation of each.

5. Weigh out a little powdered crystalline copper sulphate in a small dish. Heat gently over a small bunsen flame stirring all the time with a glass rod. Note that the blue colour disappears and that on re-weighing a loss in weight is observed. When quite cool add a few drops of water to the white solid in the dish and notice that where the water acts on the salt the original blue colour returns. (See note *d*.)

NOTES

Note a. This experiment demonstrates that water is formed by the union of two volumes of hydrogen with one volume of oxygen. No combination occurs on merely mixing the gases but on the passage of the electric spark a sharp explosion takes place and there is a considerable diminution of volume. This diminution is due to the fact that the water formed by the union of the two gases occupies a negligibly small space compared with the hydrogen and oxygen from which it is formed.

Equation for the reaction:

$$2H_2 + O_2 = 2H_2O$$

Note b. Expt. 2 shows that, at atmospheric pressure, water boils at a definite temperature which is marked as 100° on the Centigrade scale and 212° on the Fahrenheit scale. The second portion of the experiment, where brine is used, shows that here again the temperature of the vapour is the same as if pure water were being used, but the solution is considerably above that temperature. This is true for all boiling solutions, the temperature of the solution being above that of the boiling pure solvent while that of the vapour is the same in both cases.

Note c. This experiment illustrates that (1) water freezes at a definite temperature (this temperature being marked 0° on the Centigrade and 32° on the Fahrenheit thermometer), (2) that once freezing has set in, the temperature remains constant until the whole of the water has been converted into ice, and (3) that when ice melts the heat supplied from the outside is used at first only in converting the solid into liquid and not in raising the temperature, so that the temperature remains constant until the whole of the ice has melted. The second part of this experiment where strong salt solution is used shows that the addition of a soluble body to water can lower the freezing point of the solution so much that, as in the experiment, the freezing mixture is not cold enough to freeze the solution.

Note d. Expt. 5 illustrates the fact that many crystalline substances contain water as an integral part of their crystals. This water is known as *water of crystallisation* and, in the case of the copper sulphate, the large blue crystals contain five molecules of water of crystallisation to every molecule of copper sulphate and the chemical formula for the salt is consequently written $CuSO_4.5H_2O$. A salt containing water of crystallisation is spoken of as a *hydrated* salt. Water of crystallisation is generally easily driven off by gentle heating and, in coloured salts, as in this experiment, the loss of water is frequently accompanied by change of colour. The water-free salt is spoken of as an *anhydrous* salt. The anhydrous salt will generally readily take up water again and go back to the hydrated form.

IV

COMPOSITION AND PROPERTIES OF WATER (*cont.*)

1. Place a little solid caustic potash in an open dish and leave it exposed to the atmosphere for some time. Note that the surface of the caustic potash becomes coated with moisture. (See note *a.*)

2. Place in separate test-tubes equal quantities of the following substances: common salt (sodium chloride), saltpetre (potassium nitrate), gypsum (calcium sulphate) and sand. Add equal quantities of water to each test-tube, shake and note the relative quantities of each which dissolve. If all the substance does not dissolve, heat the mixture and notice if this causes more of the solid to go into solution. If all the substance does not dissolve even on heating, filter and evaporate a little of the clear solution to dryness in a porcelain dish. Note if any residue remains. (See note *b.*)

3. To a quantity of boiling water in a small beaker, add, little by little, small quantities of impure copper sulphate, until a little of the solid remains undissolved. Quickly filter the hot solution and allow the filtrate to cool slowly. Crystals of pure copper sulphate will crystallise out. (See note *c.*)

4. Filter some of the given dirty water and note that filtering takes out all the undissolved impurities and a clear filtrate is obtained. Pour a few drops of this filtrate on to a watch glass and evaporate to dryness in the steam oven Note that a residue remains.

Place the remainder of the clear filtrate in a retort and distil. Collect the distillate in a test-tube and evaporate a little to dryness in a watch glass in the steam oven. Note that in this case no residue remains. (See note *d.*)

5. Fill a small flask with boiled water and force into the neck a well-fitting cork through which passes a long, straight, narrow tube. See that the flask, when fitted with its tube, is completely full of water and that no air bubbles are trapped under the cork. Now place the flask in a water bath and gradually heat with the bunsen burner. Note that the water expands on heating and gradually rises in the narrow tube.

On cooling again the water will contract and fall once more in the narrow tube. (See note *e.*)

6. A small test-tube, sealed and full of water, is provided. Place this in a freezing mixture (a mixture of ice and salt) and allow the contained water time enough to freeze. On removing the test-tube from the freezing mixture you will probably find that the tube is cracked. (See note *f.*)

NOTES

Note a. This experiment shows that some substances can abstract water from the atmosphere. The water so abstracted is here seen as a film of moisture on the surface of the caustic potash. Substances which possess this property are termed *hygroscopic* or *deliquescent*. Among the common hygroscopic substances met with in the laboratory are caustic potash, caustic soda, calcium chloride, phosphorus pentoxide and sulphuric acid. The inclusion of this last-named substance indicates that this property is not confined to solids only.

Note b. In this experiment it will be seen that decreasing amounts of the substances dissolve as we pass from common salt at one end of the list to sand at the other end. Substances vary considerably in their solubility in water from those like salt of which large quantities will dissolve, to substances which like sand are practically insoluble in water. Obviously therefore the amounts of dissolved solids in natural waters will depend on the nature of the rocks with which the water has come in contact.

Note c. The insoluble impurities are left behind on the filter paper and pure copper sulphate crystallises out.

The size of the crystals obtained will depend on (1) the rate of cooling and (2) the amount of agitation to which the cooling solution is subjected. Rapid cooling, with constant stirring, will give small crystals, while slow cooling of an undisturbed solution will give large crystals.

Note d. This experiment illustrates the fact that filtration will only remove the insoluble impurities and that the clearness of a sample of water is no criterion of its purity. In this case the clear filtrate contains as impurities soluble salts and these can only be got rid of by distillation.

Note e. Expt. 5 shows that, starting at the ordinary temperature, water expands on heating and contracts again on cooling. This contraction of water on cooling only holds down to a temperature of 4° C. From this temperature down to 0° C. water again expands. This property of contracting down to a certain temperature and then expanding again on further cooling is peculiar to water, all other liquids contracting continuously down to their solidifying points.

Note f. This experiment illustrates the fact that water expands on solidifying to ice. The result of expansion in this case is to crack the test-tube.

V

CARBON DIOXIDE (CO_2)

1. Burn a bit of charcoal in a cylinder of oxygen or air. Pour into the cylinder a little lime water and shake. Note that the lime water becomes milky. This is a test for carbon dioxide, the gas produced when carbon combines with oxygen. (See note *a*.)

2. Breathe through a glass tube dipping into lime water diluted with twice its volume of distilled water. Note that the lime water becomes milky. This experiment demonstrates that animals breathe out carbon dioxide into the air. (See note *b*.)

3. Pour a little lime water into a watch glass and leave it exposed to the air for some time. It is soon covered with a white film and becomes milky if stirred. Air contains carbon dioxide.

4. Place sprigs of any water plant in a beaker of fresh tap water. Invert a funnel over the plant and place a test-tube full of water over the stem of the funnel. Leave in the sunlight and note that bubbles of gas are given off from the leaves and collect in the test-tube. If enough gas is obtained, remove the tube and test the gas for oxygen with a glowing splinter. Plants take in carbon dioxide from the air and break it up, retaining the carbon and liberating the oxygen. (See note *c*.)

5. Prepare carbon dioxide by the following method: Fit a wide-mouthed bottle with a cork through which pass a thistle funnel and a delivery tube bent downwards. Place some small pieces of marble in the bottle and pour in just enough water to cover the end of the thistle funnel. Add hydrochloric acid until the gas comes off rapidly. Arrange so that the end of the delivery tube passes to the bottom of a gas cylinder and in this way fill several cylinders with carbon dioxide. (See note *d*.)

(*a*) Test one cylinder with lime water and note that it becomes milky.

(*b*) Lower a lighted taper into a second cylinder and note that it goes out. (See note *e*.)

(*c*) Pour the gas from a cylinder into another empty one just as if it were water. Prove that the carbon dioxide has gone into the second cylinder by testing with lime water or a lighted taper. As it can be poured downwards carbon dioxide is heavier than air. (See note *f*.)

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NOTES

Note a. Lime water is a solution of calcium hydroxide in water. The milkiness produced is due to the reaction between the carbon dioxide gas and the calcium hydroxide with the formation of chalk (calcium carbonate). Chalk is insoluble in water and so appears as a very finely divided white solid. A solid produced in a solution in this or any similar manner is generally referred to as a *precipitate.*

Note b. The production of carbon dioxide in the body of an animal is an example of slow combustion. Food always contains carbon in combination with other elements. Animals breathe in oxygen which dissolves in the blood where it reacts with the food compounds, resulting in the production of carbon dioxide which is given out through the lungs.

Note c. Carbon dioxide is appreciably soluble in water and consequently will be contained in all samples of tap water.

Note d. Chemically, marble is calcium carbonate and has the same composition as the chalk referred to in note *a*. The hydrochloric acid liberates the carbon dioxide with the formation at the same time of water and a compound known as calcium chloride which remains dissolved in the liquid in the bottle.

Note e. This experiment shows that carbon dioxide is not capable of supporting combustion. The oxygen contained in it is firmly united with the carbon and is not available for the combustion of the taper.

Note f. The word "empty" is here used in its popular sense. The cylinder is really full of air which is replaced by the heavier carbon dioxide exactly as though water or some other liquid were poured in.

EQUATIONS

$Ca(OH)_2$	+	CO_2	=	$CaCO_3$	+	H_2O
Calcium Hydroxide (Lime water)	+	Carbon Dioxide	=	Calcium Carbonate	+	Water

$CaCO_3$	+	$2HCl$	=	$CaCl_2$	+	H_2O	+	CO_2
Calcium Carbonate	+	Hydrochloric Acid	=	Calcium Chloride	+	Water	+	Carbon Dioxide

VI

AMMONIA (NH_3)

1. Prepare ammonia gas by warming a mixture of ammonium sulphate and lime in a flask fitted with a delivery tube pointing upward. The mixture in the flask should be covered with a layer of quick lime to dry the gas as it is given off. (See note *a*.) Collect two cylinders and a flask of the gas by inverting them over the delivery tube and testing to see when they are full by means of a piece of damp red litmus held at the mouth. The cylinders and flask *must* be quite dry.

2. Dip a glass rod in strong hydrochloric acid and plunge it into a cylinder of ammonia. Note that dense white fumes are formed. (See note *b* to Chapter VII.)

3. Invert the other cylinder and push a burning taper into it. Note that the gas shows signs of burning at the mouth of the cylinder but does not allow the taper to burn in it. (See note *b*.)

4. Close the flask with a good cork through which a short piece of glass tube has been fitted. The inner end of the glass is drawn out to a fine jet. Invert the flask so that the tube dips into water coloured red with litmus and note that the water rushes into the flask, turning blue as it dissolves the ammonia gas. (See note *c*.)

5. Place a little ammonia in a small beaker with a few drops of litmus solution. Add sulphuric acid drop by drop until the litmus begins to turn red. Then add a drop or two of ammonia so that the solution just turns blue. Transfer the liquid to a porcelain dish and evaporate to dryness on a water bath. Note that a white solid is left behind (it may be tinged by the litmus). Keep the solid for the next experiment.

Repeat the experiment, using hydrochloric and nitric acids instead of the sulphuric acid, and keep the residues. (See note *d*.)

6. Take the three substances obtained in the above experiments and ignite each in turn in a small porcelain crucible over a bunsen flame. Note that in each case the substance volatilizes and goes off into the air as white fumes. No residue will be left behind. (See note *e*.)

7. Mix well (one at a time) small quantities of the following plant and animal tissues with soda lime: horn, bone meal, hair, pea meal, flour and dried milk. Heat each mixture strongly in a dry test-tube. Note that ammonia is given off in each case and may be detected both by smell and by its action on damp red litmus paper. (See note *f*.)

NOTES

Note a. Ammonia gas is collected in this way because it is both lighter than air and very soluble in water. Water dissolves about eight hundred times its volume of this gas.

Note b. That the gas shows signs of burning is due to the fact that this gas becomes inflammable when its temperature is raised considerably. Just round the taper flame the gas becomes heated and some sign of the combustion of the gas can generally be noticed. The gas does not support combustion and the taper goes out when pushed further up the cylinder.

Note c. See note c, Chapter VII, for the explanation of the similar experiment on hydrochloric acid gas. In the case of ammonia however we are dealing with an *alkaline* gas and the litmus is therefore turned from red to blue.

Note d. It will be seen later that in dealing with hydrochloric acid the blue litmus turns red. By the action of ammonia, on the contrary, red litmus is turned blue. It is very probable therefore that if hydrochloric acid solution and ammonia are mixed together there must be some point at which the mixture will turn litmus neither red nor blue. This proves to be the case. At this point one of the reagents is said to have *neutralised* the other and the resulting liquid is spoken of as being *neutral.* If at this point the solution is evaporated to dryness a new body is found to have been formed, which, in the case of this experiment, is a white solid. (It may be slightly coloured owing to the litmus used.) A substance formed in this way, by the interaction of an acid and an alkali, is known as a *salt.* (Table salt, generally spoken of as "salt," is only one of a very large number of salts.) In the experiment under consideration the salts formed are known as ammonium sulphate, ammonium chloride and ammonium nitrate respectively depending on the acid used.

Note e. This experiment illustrates the fact that all the common ammonium salts are converted, at a high temperature, into vapours and can so be driven off into the air. The importance of this in analysis will be seen later.

Note f. The production of ammonia in these experiments is due to the fact that the organic substances used contain both nitrogen and hydrogen and these two gases are given off in combination in the form of ammonia.

VII

HYDROCHLORIC ACID (HCl) AND CHLORINE (Cl_2)

Hydrochloric Acid (HCl)

1. Place some lumps of common salt (sodium chloride) in a flask fitted with a delivery tube pointing downwards. Add enough strong sulphuric acid to moisten the salt and collect two cylinders and one round-bottomed flask full of the gas. The cylinders and flask *must* be perfectly dry. (See note *a.*)

2. Plunge a lighted taper into one cylinder. The taper will be extinguished and the gas will not burn. Dip a glass rod into silver nitrate solution and hold it in the cylinder. Note the white precipitate or milkiness in the drop of liquid on the rod. Dip another glass rod into ammonia solution and hold it in the gas. Note that white fumes are formed. (See note *b.*)

3. Uncover a cylinder and leave it mouth upwards for some time. Test the gas in the cylinder with one of the tests in Expt. 2 and note that it remains in the open vessel. It is heavier than air.

4. Close the flask of gas with a good cork through which a short piece of glass rod has been fitted. Dip the tube under water coloured with blue litmus solution and shake, taking care that the end of the tube remains under water. Note that the water dissolves the gas and rises quickly in the tube to fill the flask and that the blue colour of the water changes to red. (See note *c.*)

5. Pass some hydrochloric acid gas into a little water in a test-tube. Note that it dissolves very readily. Test different portions of the solution with litmus, silver nitrate and metallic zinc and note that it behaves like the "hydrochloric acid" in the bench bottles.

Chlorine (Cl_2)

6. Place a small quantity of bleaching powder in a gas cylinder and add a little dilute sulphuric acid. Hang a bit of damp coloured rag inside the cylinder and close it with a glass plate. Note that the cylinder is gradually filled with a yellowish gas which bleaches the rag. This gas is known as chlorine.

7. Drop a little potassium permanganate solution into the third cylinder of hydrochloric acid. Note that a yellowish gas—chlorine—is produced which will bleach a piece of damp coloured rag and has a peculiar choking, pungent smell. (See note *d.*)

8. Mix a little bleaching powder with water and dip a bit of coloured rag into the mixture. Transfer the rag to some very weak sulphuric acid in a beaker and note that it is bleached immediately.

NOTES

Note a. This method of collection is adopted owing to the great solubility of hydrochloric acid gas in water. It cannot therefore be collected in the same way as hydrogen and oxygen. Carbon dioxide and hydrochloric acid gas, being much heavier than air, can be collected by "downward displacement" but whilst, in the case of the former gas, collection over water could be adopted if desired (carbon dioxide being only moderately soluble in water), this method is inadmissible with hydrochloric acid.

Note b. The experiments in Expt. 2 show that:

(1) Hydrochloric acid is not inflammable.

(2) That this gas does not support combustion.

(3) That it reacts with silver nitrate solution to give a white insoluble body (this body is known as silver chloride).

(4) That hydrochloric acid and ammonia unite to form a white compound. The ammonia used in this experiment is only a solution of ammonia gas in water. In the jar it gives off ammonia gas which unites with the hydrochloric acid to give a white solid compound known as ammonium chloride. It is this body in a very finely divided state, which appears as white fumes.

Note c. This experiment illustrates:

(1) The extreme solubility of hydrochloric acid gas in water which dissolves about four hundred and fifty times its own volume of gas.

(2) That hydrochloric acid gas, dissolved in water, gives an acid solution.

Litmus is a vegetable colouring matter which turns red with acids and blue with alkalis. As it is used to indicate the acid or alkaline nature of substances it is classed as an *indicator*. Many different indicators are used in the laboratory and several of these will be met with during the course.

Note d. The production of chlorine in this experiment depends on the breaking up of the hydrochloric acid by the permanganate. Hydrochloric acid contains both hydrogen and chlorine and the permanganate contains a large quantity of combined oxygen. Some of this oxygen unites with the hydrogen of the hydrochloric acid to form water and liberates the chlorine.

Note e. Bleaching powder is a substance formed by the union of chlorine with lime. It is readily broken up by any dilute acid, even by carbon dioxide, with the liberation of chlorine. It is much used as a ready method of storing chlorine for bleaching or disinfecting purposes. It is frequently sold under the name of "Chloride of lime."

EQUATIONS

$2NaCl + H_2SO_4$
Sodium Chloride + Sulphuric Acid
$= Na_2SO_4 + 2HCl$
= Sodium Sulphate + Hydrochloric Acid

$AgNO_3 + HCl = AgCl + HNO_3$
Silver Nitrate + Hydrochloric Acid = Silver Chloride + Nitric Acid

$K_2Mn_2O_8 + 16HCl$
Potassium Permanganate + Hydrochloric Acid
$= 2KCl + MnCl_2 + 8H_2O + 5Cl_2$
= Potassium Chloride + Manganese Chloride + Water + Chlorine

VIII

ACIDS

1. Burn a small piece of carbon in a jar of oxygen containing a little water. Cover the jar with a ground glass plate and shake well. Add a few drops of litmus to the solution produced and note that its colour is changed to red. (See note *a*.)

2. Repeat the experiment, using sulphur instead of carbon. (See note *b*.)

3. Repeat, using phosphorus as the combustible material. (See note *c*.)

4. From a siphon of sulphur dioxide pass a stream of this gas for some time into water contained in a small beaker. Divide this solution into four portions.

To the first portion add a few drops of litmus solution and note that the litmus turns red.

To the second portion add a few drops of magenta solution and note that the magenta is bleached.

To the third portion add hydrochloric acid and barium chloride solution and note that no precipitate is produced.

To the fourth portion add a few drops of strong nitric acid. Warm and then add hydrochloric acid and barium chloride solution. Note that a white precipitate is produced. (See note *d*.)

5. Drop a small quantity of phosphorus pentoxide into a little water in a beaker. Note that it reacts with the water with great vigour and completely dissolves. Divide the solution into two portions. To the first portion add a few drops of litmus solution and note that a red colour is obtained.

To the second portion add a few drops of strong nitric acid and a much larger quantity of ammonium molybdate solution. Warm and note that a yellow precipitate is formed. (See note *e*.)

NOTES

Note a. When carbon burns in oxygen, the gas carbon dioxide is formed.

$$C + O_2 = CO_2$$

Carbon + Oxygen = Carbon Dioxide

Carbon dioxide dissolves in water giving carbonic acid.

$$CO_2 + H_2O = H_2CO_3$$

Carbon Dioxide + Water = Carbonic Acid

Note b. Sulphur burns in oxygen with the production **of sulphur** dioxide gas.

$$S + O_2 = SO_2$$

Sulphur + Oxygen = Sulphur Dioxide

Sulphur dioxide dissolves in water with the production of **sulphurous** acid (not sulphuric acid).

$$SO_2 + H_2O = H_2SO_3$$

Sulphur Dioxide + Water = Sulphurous Acid

Note c. Phosphorus burns in oxygen with the production of phosphorus pentoxide, this body being seen in the gas jar in the form of white fumes. These white fumes are made up of minute particles of the white solid pentoxide.

$$4P + 5O_2 = 2P_2O_5$$

Phosphorus + Oxygen = Phosphorus Pentoxide

Phosphorus pentoxide dissolves in water with the production of phosphoric acid.

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

Phosphorus Pentoxide + Water = Phosphoric Acid

Note d. Sulphur dioxide is a gas easily liquefied by pressure and the liquid seen in the siphon is the liquefied gas. It is not a solution of the gas in water.

Sulphur dioxide is a powerful bleaching and disinfecting agent and is largely used for these purposes commercially. As pointed out in note *b*, sulphur dioxide dissolves in water giving sulphurous acid, H_2SO_3. This acid does not give a precipitate with hydrochloric acid and barium chloride. When, however, sulphurous acid is heated with nitric acid, the latter compound, being rich in oxygen, parts with some of its oxygen and oxidises the sulphurous acid to sulphuric acid.

$$H_2SO_3 + O = H_2SO_4$$

Sulphurous Acid + Oxygen = Sulphuric Acid

• Sulphuric acid reacts with barium chloride to give an insoluble white compound, barium sulphate, which comes down as white precipitate.

H_2SO_4 + $BaCl_2$
Sulphuric Acid + Barium Chloride
= $BaSO_4$ + $2HCl$
= *Barium Sulphate* + Hydrochloric Acid

Note e. For the formation of phosphoric acid from phosphorus pentoxide, see note *c.* Phosphoric acid reacts with ammonium molybdate, in the presence of nitric acid, with the production of a yellow precipitate of ammonium phospho-molybdate.

$$2(NH_3)_3PO_4.22MoO_3.12H_2O$$

General note. It is to be noted that all the substances which, on burning, gave oxides which form acids with water, are non-metals. This should be remembered in distinction to the behaviour of the metallic oxides dealt with in another chapter. The metals on burning gave basic oxides, while the non-metals gave acid oxides.

IX

ACIDS (*cont.*). NITRIC ACID

1. Place a little sodium nitrate in a small retort and pour in enough sulphuric acid to cover it. Heat gently and collect the liquid which distils over in a small flask. Add to it an equal volume of water and compare the properties of this liquid with the nitric acid on the bench. Note that (*a*) both turn litmus red, (*b*) both give a brown colour when poured into a test-tube containing ferrous sulphate solution, (*c*) both give off brown fumes when warmed with copper turnings, (*d*) both turn a bit of coagulated white of egg yellow. (See note *a*.)

2. Heat a little powdered sodium nitrate in a test-tube until it melts and then drop into the molten mass a small piece of glowing charcoal. Note that the charcoal burns brightly in the melted nitrate. (See note *b*.)

3. Heat a little powdered lead nitrate in a test-tube. Note that it gives off red fumes of nitrogen peroxide. Prove that oxygen is given off at the same time by testing the gas in the tube with a glowing splinter of wood. (See note *c*.)

4. Boil some sodium hydroxide solution in a flask and add to it some bits of zinc or aluminium foil. To the boiling mixture add a small quantity of sodium nitrate and test the steam with litmus paper for the presence of ammonia. (See note *d*.)

5. Fill three Nessler cylinders to the mark with rain water, surface water and deep well water respectively. Add to each a little Nessler solution and stir with a clean glass rod. Note that the rain water and the surface water both give a faint yellow colour whilst the deep well water remains colourless. (See note *e*.)

6. Wash three test-tubes very carefully with distilled water. Put into them 1 c.c. of rain water, surface water and deep well water respectively. Add to each about 3 c.c. of pure strong sulphuric acid, shake to mix the liquids and cool under the tap. Then add to each about 1 c.c. of carbazol solution. Note that a green colour appears in each tube but that the colour is deeper in the surface water than in the rain water and that it is still deeper in the deep well water. (See note *f*.)

NOTES

Note a. The sodium nitrate is acted upon by the sulphuric acid with the production of sodium hydrogen sulphate and nitric acid.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

Sodium Nitrate + Sulphuric Acid = Sodium Hydrogen Sulphate + Nitric Acid

Under certain circumstances the reaction may go further and normal sodium sulphate be formed instead of the hydrogen sulphate.

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$$

Sodium Nitrate + Sulphuric Acid = Sodium Sulphate + Nitric Acid

The dark brown colour produced when nitric acid acts on ferrous sulphate is a compound of nitric oxide, which comes from the nitric acid and ferrous sulphate, and has the composition $FeSO_4.NO$. This compound is broken up by heat, the nitric oxide gas being liberated, and this can be shown by gently warming the tube. This brown compound will be met with again in the "brown ring test" for nitrates.

Nitric acid acts on copper with the production of nitric oxide, NO, and this combines with oxygen from the air to give nitrogen peroxide, NO_2.

This latter gas forms the dark red fumes which are observed.

White of egg belongs to the class of organic substances known as proteins. The yellow colour nitric acid gives with egg white is given by many other proteins. The reaction will be met with again later.

Note b. Nitric acid and the nitrates are bodies which contain a high percentage of oxygen, as can be seen by examining their formulae. In this experiment the molten nitrate parts with a portion of its oxygen and this unites with the carbon to give carbon dioxide, CO_2, which escapes as a gas from the test-tube.

Note c. Lead nitrate breaks up on heating giving rise to nitrogen peroxide, oxygen and lead oxide. The last named body remains behind as a yellowish solid in the test-tube.

$$Pb(NO_3)_2 = PbO + 2NO_2 + O$$

Lead Nitrate = Lead Oxide + Nitrogen Peroxide + Oxygen

Note d. Zinc or aluminium react with sodium hydroxide solution (caustic soda) with the liberation of hydrogen. This hydrogen reacts with the nitrate, taking away the oxygen of the nitrate and forming ammonia, NH_3. This reaction will be met with again later on.

Note e. Nessler solution is an alkaline solution of mercuric iodide in potassium iodide. It is a very delicate reagent for ammonia, giving

a yellowish or brownish colour with mere traces of this compound, due to the formation of small quantities of the brown compound $(NH_2Hg)I.HgO$. Nessler solution should only be used to detect very small quantities of ammonia, for if larger quantities be present, the brown compound is thrown down as a precipitate and no estimate of the quantity of ammonia present can then be made.

Note f. Carbazol is an organic substance with the composition $(C_6H_4)_2.NH$. It gives with even small quantities of nitrates a green colouration, the depth of the colour depending on the quantity of nitrate present.

X

BASES

1. Heat a small piece of metallic calcium on a piece of thin sheet iron. Note that it burns and leaves behind a white residue. When cool put this white residue into water, shake up well and filter. Test both the residue on the filter paper and the filtrate with red litmus paper which will be turned blue. Breathe through a glass tube into the filtrate and note that it turns milky. (See note *a*.)

2. Burn a small piece of magnesium ribbon and catch the white ash produced in a porcelain dish. Moisten the ash with water and test it with a piece of red litmus paper. Note that the red litmus paper turns blue. (See note *b*.)

3. Place a small piece of metallic calcium in a test-tube and add water. Note that a gas is given off which shows the characteristics of hydrogen. Note that a white substance is left floating about in the water after the calcium has disappeared. Filter this white substance off and test both the white solid on the filter paper and the clear filtrate with red litmus paper. Note that the red litmus turns blue. Breathe through a glass tube into the clear filtrate and note that a milkiness is produced. (See note *c*.)

4. Put a lump of quick lime in a dish and pour over it a small quantity of water. Note that the lime quickly begins to get hot and that the water disappears. At the same time the lime swells and crumbles to powder. (See note *d*.)

5. Take a little of the powder produced in Expt. 4, in a test-tube, add water and shake up well. Filter and test the filtrate with red litmus paper. Note that the red litmus paper turns blue. Now breathe through a glass tube into the clear filtrate and note that a milkiness is produced. (See note *e*.)

6. Add a *very small* quantity of metallic sodium to a quantity of distilled water in a porcelain dish. Note that a vigorous action takes place and on testing the solution left in the dish, it turns red litmus paper blue. (See note *f*.)

NOTES

Note a. In this experiment the calcium, in burning, unites with the oxygen of the air to give calcium oxide (quick lime).

$$\underset{\text{Calcium}}{Ca} + \underset{\text{Oxygen}}{O} = \underset{\text{Calcium Oxide}}{CaO}$$

When the calcium oxide is shaken up with water it unites with the water to give calcium hydroxide (slaked lime) and a portion of this dissolves in the water.

$$\underset{\text{Calcium Oxide}}{CaO} + \underset{\text{Water}}{H_2O} = \underset{\text{Calcium Hydroxide}}{Ca(OH)_2}$$

The calcium hydroxide dissolved in the water reacts with the carbon dioxide of the breath giving insoluble calcium carbonate, which appears in the form of a very fine precipitate and gives rise to the milkiness observed.

$$\underset{\text{Calcium Hydroxide}}{Ca(OH)_2} + \underset{\text{Carbon Dioxide}}{CO_2} = \underset{\text{Calcium Carbonate}}{CaCO_3} + \underset{\text{Water}}{H_2O}$$

Note b. The magnesium, in burning, is converted into magnesium oxide and a small quantity of this dissolves in the water forming an alkaline solution.

$$\underset{\text{Magnesium}}{Mg} + \underset{\text{Oxygen}}{O} = \underset{\text{Magnesium Oxide}}{MgO}$$

Note c. In a previous chapter it has been shown that water is a compound of oxygen and hydrogen. In Expt. 3 the calcium liberates the hydrogen from the water and unites with the oxygen with the formation of calcium oxide.

$$\underset{\text{Calcium}}{Ca} + \underset{\text{Water}}{H_2O} = \underset{\text{Calcium Oxide}}{CaO} + \underset{\text{Hydrogen}}{H_2}$$

The calcium oxide then passes through the same series of reactions in this experiment as in Expt. 1. (See note *a.*)

Note d. This experiment shows the great vigour of the reaction between calcium oxide (quick lime) and water to form calcium hydroxide (slaked lime). The energy liberated in the reaction appears in the form of heat and frequently, with good samples of lime, the temperature rises so much that the water boils.

$$\underset{\text{Calcium Oxide}}{CaO} + \underset{\text{Water}}{H_2O} = \underset{\text{Calcium Hydroxide}}{Ca(OH)_2}$$

Note e. The reactions in this experiment are the same as those taking place in the latter part of Expt. 1. (See note *a.*)

Note f. The sodium reacts with the water in a similar way to calcium, liberating hydrogen and forming sodium hydroxide (caustic soda), which, being very soluble in water, remains dissolved in the water and does not separate as a precipitate like the calcium oxide in Expt. 1.

$$2Na + H_2O = 2NaOH + H_2$$

Sodium + Water = Caustic Soda + Hydrogen

The reaction is so vigorous that only a very small quantity of sodium should be used and the face should be kept away from the dish.

A similar reaction, still more vigorous, takes place with potassium and water with the formation of caustic potash and hydrogen.

$$2K + H_2O = 2KOH + H_2$$

Potassium + Water = Caustic Potash + Hydrogen

General note. It is to be noticed that in all these experiments the oxide of a metal is produced and that all these metallic oxides act as bases, this being shown by the fact that they turn red litmus blue. A small number of these bases, particularly caustic soda and caustic potash, are given a special name and are termed alkalis.

XI

SALTS

1. Place about 10 c.c. of caustic soda solution in a small evaporating dish. To this add, drop by drop, dilute hydrochloric acid, taking out every now and again a drop of the liquid on the end of a glass rod and testing it on blue litmus paper. At first the blue litmus paper will be unaltered but a point will be at last reached when the paper will be turned pink. At this point evaporate the solution in the dish nearly to dryness over the bunsen flame and finish the drying on a water bath. A white compound, sodium chloride (common salt), will have been formed by the reaction between the caustic soda solution and the hydrochloric acid. Test this white compound for sodium by holding some of it on a wire in the bunsen flame and noting the yellow colouration obtained and for chloride by dissolving some of it in water, adding nitric acid and silver nitrate, and noting the white precipitate obtained

2. Repeat the previous experiment but use dilute sulphuric acid instead of hydrochloric acid. In this case the white compound produced is sodium sulphate and this should be confirmed by testing for sodium as in the previous experiment and for sulphate by adding to a solution of the solid in water hydrochloric acid and barium chloride solution, a white precipitate being obtained.

3. Repeat, using in this case dilute nitric acid. Here sodium nitrate will be the white solid obtained and this should be confirmed by testing as before for sodium and for nitrate by adding to a solution of the solid, ferrous sulphate solution and, slowly, down the side of the test-tube, strong sulphuric acid. The sulphuric acid will run to the bottom of the test-tube as a separate layer and where the liquids meet, the formation of a brown ring will show the presence of a nitrate.

4. Put into a beaker a strong solution of potassium hydroxide (caustic potash). Pour into it dilute sulphuric acid a few drops at a time until a drop of the mixture on a glass rod ceases to turn a bit of red litmus paper blue. Now cool the mixture and note that white crystals of potassium sulphate separate out. Test these for potassium, by introducing some into the flame and noting the lilac colouration produced and for sulphate as described in Expt. 2.

5. To a little dilute sulphuric acid in a beaker add iron filings until no more will dissolve on boiling. Note that hydrogen is given off. Filter the solution while hot and then cool down the filtrate. Note that light green crystals of ferrous sulphate will crystallise out.

6. Repeat Expt. 5, using granulated zinc instead of iron filings. In this case the hot filtered solution should be boiled down to a small bulk before cooling, when crystals of zinc sulphate will crystallise out.

7. Put a small piece of zinc into a test-tube containing nitric acid. Note that although a reaction takes place, hydrogen is not given off but oxides of nitrogen are evolved instead. Pour a little of the solution into a watch glass and allow it to evaporate. Note that a crystalline salt is formed. (See general note.)

NOTE

General note. All the experiments in this chapter are examples of the production of salts. A salt can be formed by either:

(*a*) the reaction between an acid and a base, or

(*b*) the replacement of the hydrogen of an acid by a metal.

In the case of (*a*) the correct quantity of acid to be added to the base is shown by the action of an indicator, in this case litmus. Since bases turn litmus blue, while alkalis turn litmus red, there will be, in the addition of an acid to a base, some point at which the liquid will turn litmus neither red nor blue, that is, will be without effect on litmus. At this point the acid and base are said to have *neutralised* one another and it can be shown by experiment that the salt produced is a *neutral* body, that is it has no action on litmus.

In Expts. 1, 2, 3 and 4 the salts produced are sodium chloride, sodium sulphate, sodium nitrate and potassium sulphate respectively. These are produced according to the following equations:

$$NaOH + HCl = NaCl + H_2O$$
Caustic Soda + Hydrochloric Acid = Sodium Chloride + Water

$$2NaOH + H_2SO_4 = Na_2SO_4 + H_2O$$
Caustic Soda + Sulphuric Acid = Sodium Sulphate + Water

$$NaOH + HNO_3 = NaNO_3 + H_2O$$
Caustic Soda + Nitric Acid = Sodium Nitrate + Water

$$2KOH + H_2SO_4 = K_2SO_4 + H_2O$$
Caustic Potash + Sulphuric Acid = Potassium Sulphate + Water

Note that in all cases the production of the salt is accompanied by the formation of water.

The explanation of the analytical reactions used in testing the salts has been given in previous chapters.

In Expts. 5 and 6, salts are produced by method (*b*). Here the metal replaces the hydrogen of the acid and the gas comes off while the salt is left in solution. The reactions in the two examples given are explained by the following equations:

$$Fe + H_2SO_4 = FeSO_4 + H_2$$
Iron + Sulphuric Acid = Iron Sulphate + Hydrogen
(Ferrous Sulphate)

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
Zinc + Sulphuric Acid = Zinc Sulphate + Hydrogen

In Expt. 7 no hydrogen is evolved although a salt is formed as with other acids. This is general where nitric acid is used and it may be considered to be due to the strong oxidising action of nitric acid, which oxidises the hydrogen which would be evolved, to water. The reaction which takes place is given by the equation

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$$
Zinc + Nitric Acid = Zinc Nitrate + Nitrous Oxide + Water

XII

SALTS (*cont.*)

1. Measure out with a pipette 10 c.c. of a solution of sulphuric acid containing 1 gr. of the pure acid in 100 c.c. of solution. The 10 c.c. will therefore contain 0·1 gr. of pure sulphuric acid. Run the 10 c.c. into a beaker, add a few drops of litmus and run in from a burette sodium hydroxide solution, containing 1 gr. of pure sodium hydroxide in 100 c.c., until the red colour of the litmus just changes to purple. Note the volume required to produce this change. Calculate the weight of sulphuric acid which neutralises 40 grs. of sodium hydroxide. Now evaporate the solution to dryness and note that a white residue of sodium sulphate is left. This can be tested, if desired, as in the preceding chapter.

2. Repeat Expt. 1 using 1 per cent. hydrochloric acid in place of sulphuric acid. Calculate the weight of hydrochloric acid required to neutralise 40 gms. of sodium hydroxide.

3. Repeat Expt. 1 using 1 per cent. nitric acid in place of sulphuric acid. Calculate the weight of nitric acid required to neutralise 40 grs. of sodium hydroxide.

4. Repeat Expt. 1 using sulphuric acid and sodium hydroxide solution as before but phenol-phthalein as the indicator instead of litmus. This indicator is colourless with acids and bright red with alkalis.

5. Repeat Expt. 1 using again 1 per cent. sulphuric acid but using 1 per cent. ammonia solution as the alkali and methyl orange as the indicator. This indicator is pink with acids and yellow with alkalis. Calculate the weight of sulphuric acid which neutralises 17 grs. of ammonia. (See general note.)

NOTE

General note. Most of the reactions occurring in these experiments have been given in the preceding chapter but they are repeated here for convenience.

(1) $2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$.

(2) $NaOH + HCl = NaCl + H_2O$.

(3) $NaOH + HNO_3 = NaNO_3 + H_2O$.

(4) $2NH_3 + H_2SO_4 = (NH_4)_2SO_4$.

The results obtained can be checked by calculation and the method of doing this is shown in the following example. Take the case of the neutralisation of hydrochloric acid by caustic soda. The equation must first of all be written down and the molecular weight of each compound taking part in the reaction be found by adding together the atomic weights of the elements contained therein.

$$\begin{array}{ccccccc} NaOH & + & HCl & = & NaCl & + & H_2O \\ 23 + 16 + 1 & & 1 + 35{\cdot}5 & & 23 + 35{\cdot}5 & & (2 \times 1) + 16 \end{array}$$

Mol. wt. NaOH = 40; Mol. wt. HCl = 36·5; Mol. wt. NaCl = 58·5; Mol. wt. H_2O = 18. Thus it is seen that 40 grs. of sodium hydroxide neutralise 36·5 grs. of hydrochloric acid.

The other reactions can be worked out similarly, remembering that sulphuric acid contains two replaceable hydrogen atoms.

The following atomic weights will be needed:

$$H = 1, \quad O = 16, \quad N = 14, \quad Cl = 35{\cdot}5, \quad S = 32, \quad Na = 23$$

The suitable choice of an indicator will be learnt by experience. In any reaction between a solution of a metallic hydroxide and an acid either litmus or phenol-phthalein may be used but in any reaction involving ammonia methyl orange must be used. Other special cases will be met with later on.

XIII

EQUIVALENTS

1. Fill a graduated tube with dilute hydrochloric acid and invert it in a dish of the same liquid. Place a bit of magnesium in a small test-tube filled with water and push it into the bottom of the measuring tube. As the acid diffuses into the small test-tube gas is given off. When all the gas has come off transfer the tube to a deep vessel so that the liquid inside and outside the tube can be adjusted to the same level. Read the volume of gas and correct it to standard temperature and pressure (0° C. and 760 mm.) as follows:

$$\frac{\text{Volume of gas} \times 273 \times h}{(273 + t) \times 760} = \text{volume at N.T.P.},$$

where h = height of barometer in millimetres and t = the temperature in degrees Centigrade.

Calculate the weight of magnesium required to displace 1 gr. of hydrogen from the acid. One litre of hydrogen weighs 0·0896 gr.

2. Repeat the experiment using zinc instead of magnesium. Calculate the weight of zinc required to displace 1 gr. of hydrogen from the acid.

3. Repeat Expt. 1 using dilute sulphuric acid instead of dilute hydrochloric acid.

4. Weigh a small porcelain crucible. In it place a quantity of magnesium, about 0·5 gr., divided into small pieces and weigh again. The difference in weights will give the exact amount of magnesium taken. Almost cover the crucible with a lid and heat strongly over the bunsen flame. From time to time remove the flame, allow the crucible to cool down slightly and examine the magnesium to see whether the whole has been converted into oxide. When this has taken place allow to cool and weigh again. All weighings must be done with the greatest possible accuracy. The increase in weight after the magnesium has been burnt gives the amount of oxygen which has combined with the weighed quantity of magnesium. Knowing this quantity and the equivalent of magnesium found in Expt. 1, calculate the equivalent of oxygen. (See general note.)

NOTE

General note. The chemical equivalent of an element can be defined as the amount of that element which will combine with, or, by substitution, displace from a compound, one part by weight of hydrogen. In Expts. 1, 2 and 3 the equivalents of magnesium and zinc are found by making these elements displace the hydrogen from an acid. The volume of hydrogen is measured and the weight of this volume found from the data given. Knowing the weight of metal taken and the weight of hydrogen displaced, the equivalent can be calculated.

The formula given for the correction of gas to normal temperature and pressure (N.T.P.) is a direct deduction from Boyle's Law and Charles' Law (dealt with in Chapter XXXVII) and its correctness should be checked with these laws in mind. The weight of one litre of hydrogen is a very important figure and must be committed to memory.

Occasionally the equivalent of an element is determined indirectly. In Expt. 4 the weight of oxygen combining with a given weight of magnesium is found. Expt. 1 has already given the weight of magnesium which will replace 1 gr. of hydrogen, so the data now obtained can be used to calculate the weight of oxygen which will combine with 1 gr. of hydrogen.

XIV

STANDARD SOLUTIONS

1. With the deci-normal solution of sulphuric acid provided, determine the number of grams of caustic soda in 100 c.c. of the given solution. Use phenol-phthalein as an indicator, adding a few drops to a measured quantity, say 20 c.c., of the caustic soda in a beaker and running in the standard sulphuric acid very slowly from a burette until the colour change is obtained. Phenol-phthalein is colourless with acids and red with alkalis.

2. Carry out a similar determination of the strength of the given sulphuric acid, using deci-normal caustic soda in the burette and phenol-phthalein as indicator.

3. Find the strength, stated in grams per 100 c.c., of the given ammonia solution using the deci-normal solution of sulphuric acid in the burette and methyl orange as indicator. Methyl orange is yellow with alkalis and pink with acids.

4. Determine the strength, stated in grams per 100 c.c., of the lime water on the bench, using deci-normal hydrochloric acid in the burette. Phenol-phthalein should be used as indicator.

5. Determine the strength, stated in grams per 100 c.c., of the given sodium carbonate solution, using either deci-normal sulphuric or deci-normal hydrochloric acid in the burette. Methyl orange should be used as indicator. (See general note.)

NOTE

General note. It will be necessary in carrying out these determinations to remember exactly what the term "normal" or "deci-normal" solution means. A normal solution can be defined as a solution containing one gram of hydrogen, or its equivalent, per litre. Thus with hydrochloric acid, whose formula is HCl, it will be necessary to have 36·5 grs. of hydrochloric acid in one litre in order to have a normal solution of this acid, since the molecule of hydrochloric acid contains only one hydrogen atom, and the molecular weight of this acid is 36·5. (H = 1, Cl = 35·5.)

In a similar way with nitric acid, it will be necessary to have 63 grs. of this substance to the litre, since again only one hydrogen atom is present in the molecule, HNO_3, and the molecular weight is 63. (H = 1, N = 14, O = 3 × 16 = 48.)

In sulphuric acid however, where there are two hydrogen atoms in the molecule, H_2SO_4, it will only be necessary to have half the molecular weight in grams to the litre to obtain a normal solution. That is, there will be 49 grs. of this acid to the litre. (H = 2 × 1 = 2, S = 32, O = 16 × 4 = 64. Molecular weight = 2 + 32 + 64 = 98. This divided by 2 gives 49.)

Normal caustic soda solution will contain the full molecular weight of caustic soda, NaOH, to the litre, since here we are concerned with the sodium atom in the molecule and one sodium atom is equivalent to one hydrogen atom. Thus normal caustic soda will contain 40 grs. of caustic soda per litre. (Na = 23, O = 16, H = 1. Molecular weight = 40.)

Normal sodium carbonate solution however, since sodium carbonate, Na_2CO_3, contains two atoms of sodium in the molecule, will contain half the molecular weight in grams to the litre. That is 53 grs. per litre. (Na = 2 × 23 = 46, C = 12, O = 3 × 16 = 48. Molecular weight = 106. This divided by 2 gives 53.)

Bearing the above in mind and writing down the equations for each reaction, as shown in Chapter XII, it will be easily seen that the required strength of the solutions in the experiments can be worked out.

The letter "N" is generally used instead of the word "normal." Thus normal sulphuric acid will frequently be found labelled "N. H_2SO_4."

A deci-normal solution is one which is one-tenth the strength of a normal solution. It is frequently referred to as an "N/10" solution. Thus deci-normal sulphuric acid may be labelled "N/10 H_2SO_4."

XV

STANDARD SOLUTIONS (*cont.*)

1. With the given deci-normal silver nitrate estimate the weight of sodium chloride in 100 c.c. of the solution provided.

A definite quantity of the chloride solution, say 25 c.c., is measured out by means of a pipette and transferred to a small porcelain dish. A few drops of potassium chromate solution are added to act as an indicator. The standard silver nitrate solution is then run in cautiously from a burette, the solution in the dish being constantly stirred with a rod, until the yellow colour caused by the chromate becomes changed to a reddish tinge, due to the formation of a small quantity of red silver chromate. Carry out two or three titrations and take the mean value. From the amount of standard silver nitrate used calculate the amount of sodium chloride in the given solution. (See note *a*.)

2. With the deci-normal potassium permanganate provided estimate the amount of ferrous sulphate in the given solution. With a pipette measure out 25 c.c. of the given iron solution into a beaker. Add about 10 c.c. of dilute sulphuric acid and run in the standard permanganate solution from a burette until a permanent pink shade is produced. The solution in the beaker should be constantly stirred with a glass rod while the permanganate is being run in. Carry out two or three titrations and take the mean value. From the amount of permanganate used, calculate the amount of ferrous sulphate in the given solution. (See note *b*.)

NOTES

Note a. Since the precipitation of chloride is here aimed at and this element is precipitated in the form of silver chloride, ($AgCl$), the element in the silver nitrate to be considered in preparing a standard solution of silver nitrate will be the silver. Silver nitrate has the composition $AgNO_3$, that is it contains only one atom of silver in the molecule and, since one atom of silver is equivalent to one atom of hydrogen, a normal solution of silver nitrate will contain the full molecular weight of silver nitrate in a litre of solution. That is, it will contain 170 grs. of silver nitrate in the litre. ($Ag = 108$, $N = 14$, $O = 16 \times 3 = 48$, $AgNO_3 = 108 + 14 + 48 = 170$). A deci-normal solution will contain a tenth of this weight—17 grs. per litre.

The reaction which goes on in the estimation is as follows:

$$AgNO_3 \quad + \quad NaCl \quad = \quad AgCl \quad + \quad NaNO_3$$

Silver Nitrate + Sodium Chloride = Silver Chloride + Sodium Nitrate

The silver is completely removed from the solution as a white precipitate before the chromate which has been added is acted upon. When the reaction with the chloride is complete, red silver chromate begins to be formed and thus the formation of a reddish tint marks the end of the reaction which is to be considered.

Note b. In this estimation the permanganate is used as an oxidising agent to oxidise iron in the ferrous state to iron in the ferric state. Potassium permanganate, $K_2Mn_2O_8$, will react with ferrous sulphate under suitable conditions (the presence of sulphuric acid) and will oxidise it to ferric sulphate according to the following equation:

$$K_2Mn_2O_8 \quad + \quad 10FeSO_4 \quad + \quad 8H_2SO_4$$

Potassium Permanganate + Ferrous Sulphate + Sulphuric Acid

$$= \quad K_2SO_4 \quad + \quad 2MnSO_4 \quad + \quad 8H_2O$$

= Potassium Sulphate + Manganese Sulphate + Water

$$+ \quad 5Fe_2(SO_4)_3$$

+ Ferric Sulphate

That is, 316 grs. of Potassium Permanganate ($K = 39 \times 2 = 78$, $Mn = 55 \times 2 = 110$, $O = 16 \times 8 = 128$, $K_2Mn_2O_8 = 316$) will oxidise 1520 grs. of Ferrous Sulphate ($Fe = 56$, $S = 32$, $O = 64$, $FeSO_4 = 152$, $10FeSO_4 = 1520$).

From the above data and knowing that deci-normal potassium permanganate contains 3·16 grs. K_2MnO_8 per litre the amount of ferrous sulphate present can be calculated from the results of the titrations.

The solution remains colourless as long as any ferrous sulphate is being oxidised but, directly this has been completed, the first slight excess of permanganate gives its own red tint to the solution and the reaction is known to be at an end.

XVI

METALS

1. Examine specimens of different metals (iron, copper, aluminium, calcium, magnesium, sodium and potassium).

2. Dissolve a piece of iron wire in dilute sulphuric acid. Note that hydrogen is given off and a pale green solution is produced which contains iron sulphate. Black flakes of impurity may be left.

3. To a little of the solution from (2) add a few drops of nitric acid and boil. Note that red fumes are given off, and the solution changes in colour from green to brownish-yellow. (See note *a.*)

4. To different portions of the green and the brownish-yellow solutions add ammonia, potassium ferrocyanide and potassium sulphocyanide. Note the differences in the precipitates as follows:

Reagent added	Greenish solution	Brownish-red solution
Ammonia	White ppt. turning green	Brown ppt.
Potassium ferrocyanide	Light blue ppt.	Dark blue ppt.
Potassium sulphocyanide	No colour	Blood red colour

5. Dissolve a small piece of aluminium in hydrochloric acid. To a portion of the solution add ammonia. Note that a white precipitate is formed. To another portion add soda solution. Note that a white precipitate is produced which dissolves as more soda is added. (See note *c.*)

6. Prepare a solution of calcium chloride by dissolving lime in hydrochloric acid. Add ammonia and note that a white precipitate of calcium hydrate appears. (The solution must be strong.) Add ammonium chloride and note that the precipitate is dissolved. (See note *d.*)

7. Place bits of chalk, limestone and marble in separate test-tubes and dissolve in hydrochloric acid. Note that in each case carbon dioxide is given off (tested by holding a rod dipped in lime water in the neck of each tube.)

Test the solutions for calcium by adding ammonium carbonate which gives a white precipitate. Filter the precipitates, wash and redissolve in acetic acid. Add ammonium oxalate to the clear solutions and note the white precipitates of calcium oxalate formed in each case. (See note *e.*)

8. Dissolve a bit of magnesium ribbon in hydrochloric acid. Divide the solution obtained into two portions. To one add ammonia, to the *other ammonium carbonate. Note that there is a white precipitate* in both cases. Add ammonium chloride solution. Note that the precipitates are dissolved. (See note *f*.)

9. Heat a little commercial sodium carbonate or "washing soda" as it is termed. Note that water is given off and a white powder of sodium carbonate left behind. (See note *g*.)

10. Heat a little sodium bicarbonate in a test-tube. Note that water and carbon dioxide are given off and that sodium carbonate is left as a residue. (See note *h*.)

11. Heat some ammonium salts in test-tubes. Note that they all sublime and leave no residue.

NOTES

Note a. When iron is acted on by a mineral acid such as sulphuric a salt is produced which goes into solution and hydrogen is liberated. The common metals fall into two classes with regard to their behaviour towards acids:

(*a*) Silver, lead, mercury, copper.

(*b*) Iron, aluminium, zinc, manganese, barium, calcium, magnesium, potassium, sodium.

Strong or dilute hydrochloric acid or dilute sulphuric acid have no appreciable action on Group (*a*) metals; but dissolve Group (*b*) metals, hydrogen being given off in each case, e.g. $Mg + H_2SO_4 = MgSO_4 + H_2$.
Strong hot sulphuric acid will dissolve Group (*a*) metals, sulphur dioxide being given off, e.g. $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$.
Nitric acid (either strong or dilute) acts on metals of both Groups (*a*) and (*b*) (with the exception of aluminium), forming a nitrate and liberating nitrogen oxides by the reduction of some of the acid. Iron is not affected by strong nitric acid; but is readily dissolved by dilute. The reactions vary according to the concentration of the nitric acid which of course varies as the reaction proceeds, e.g.

(Strong nitric acid) $Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$
(Dilute ,, ,,) $2Cu + 6HNO_3 = 2Cu(NO_3)_2 + N_2O_3 + 3H_2O$
(More ,, ,, ,,) $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$
(Very ,, ,, ,,) $4Cu + 10HNO_3 = 4Cu(NO_3)_2 + N_2O + 5H_2O$

When a metal has more than one valency, two series of salts can be formed. These are known as the -ic salts (higher valency) and -ous salts (lower valency).
When a metal is acted on by an acid the salt with the lower valency is usually formed.
Iron can function as a ter-valent (3) or bi-valent (2) metal so that when iron and sulphuric acid react the -ous salt will be formed. $Fe + H_2SO_4 = FeSO_4 + H_2$. This is known as ferrous sulphate. Nitric acid is a strong oxidising agent and raises the salt to the -ic state where iron is ter-valent, some of the nitric acid being itself reduced.

$$3FeSO_4 + 4HNO_3 = Fe_2(SO_4)_3 + Fe(NO_3)_3 + NO + 2H_2O$$

When nitric acid acts on a metal like iron the ferric salt will be produced finally for if the -ous salt was first formed it would be immediately converted to the ferric state.

Note b. It will be observed that ferric and ferrous salts have quite different colours and reactions and this affords a ready means of identification.

$$FeSO_4 + 2NH_4OH = (NH_4)_2SO_4 + Fe(OH)_2$$
(ferrous hydrate, greenish)

$$Fe_2(SO_4)_3 + 3NH_4OH = 3(NH_4)_2SO_4 + 2Fe(OH)_3$$
(ferric hydrate, brown)

$$K_4Fe(CN)_6 + FeSO_4 = K_2SO_4 + FeK_2Fe(CN)_6$$
(light blue precipitate)

$$3K_4Fe(CN)_6 + 2Fe_2(SO_4)_3 = 6K_2SO_4 + Fe_4(Fe(CN)_6)_3$$
(dark blue precipitate).

Note c. Aluminium chloride is formed and the addition of ammonia brings down the hydrate.

$$Al_2Cl_6 + 6NH_4OH = Al_2(OH)_6 + 6NH_4Cl$$

The same hydrate is produced when soda is added to the aluminium chloride solution, but $Al_2(OH)_6$ is soluble in excess of soda. The hydrate is reprecipitated by ammonium chloride.

Note d. Ammonia precipitates calcium hydrate ($Ca(OH)_2$) which is redissolved in the ammonium chloride. This reaction is of importance in analytical chemistry as it allows separations to take place which would otherwise be impossible. For instance, if a soluble calcium and an iron salt were present together in a strong solution the addition of ammonium chloride before adding the ammonia would keep the calcium in solution while the iron hydrate would be precipitated.

Note e. Chalk, limestone and marble are all carbonates of calcium and therefore can be decomposed by any acid, e.g. HCl.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

The addition of ammonium carbonate reprecipitates the calcium as calcium carbonate.

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$$

The acetic acid decomposes the calcium carbonate exactly as the hydrochloric acid.

$$CaCO_3 + 2CH_3COOH = (CH_3COO)_2Ca + CO_2 + H_2O$$

The calcium acetate is soluble and the addition of ammonium oxalate precipitates the calcium as the insoluble calcium oxalate.

$$(CH_3COO)_2Ca + (COONH_4)_2 = (COO)_2Ca + 2CH_3COONH_4$$

Note f. Those reactions again show the importance of ammonium chloride. $Mg(OH)_2$ and $MgCO_3$ are insoluble in water but soluble in ammonium chloride solution so that if ammonium carbonate is added alone calcium and magnesium would both be precipitated as insoluble carbonates. The addition of ammonium chloride keeps the magnesium in solution and allows a separation to be made.

Note g. Sodium carbonate is sold commercially as "soda crystals" or "washing soda." The crystals are only formed with the addition of water; this is known as "water of crystallisation." Heat drives the water off and a white powder of sodium carbonate less the water results. This is known as an "anhydrous" salt. "Soda" crystals have the composition $Na_2CO_3 10H_2O$ while anhydrous soda carbonate is Na_2CO_3. The water of crystallisation is not included in a formula unless it is desired to weigh a substance accurately when it must be allowed for.

Note h. Sodium bicarbonate or acid sodium carbonate is a salt in which only half the hydrogen of the acid is replaced by sodium. On heating, CO_2 and water are given off and sodium carbonate is left.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

XVII

PRELIMINARY TESTS FOR BASES

1. Take one of the salts provided and examine it in the following way. (The substance may be in solution or as a solid. If it is in solution, evaporate a little to dryness to obtain some in the solid state.)

(*a*) Solubility in water or in acids.

(*b*) Colour (blue, white, green, pink, etc.).

(*c*) Condition (fine or coarse crystals, dry or damp, etc.).

(*d*) Reaction to litmus (acid or alkaline). (See note *a*.)

2. Take a little of the dry substance and heat it in a test-tube. A sublimate indicates an ammonium salt or a mercury compound. (See note *b*.)

3. Heat a little of the solid with soda lime, ammonia given off (tested with a piece of damp litmus paper) indicates an ammonium salt or organic matter. Should ammonia be given off and the substance char on heating, shake some of the original substance up with water, filter and test the solution by heating with caustic soda solution. If ammonia is given off the presence of an ammonium salt is confirmed. (See note *c*.)

4. Take a little of the solid on a piece of platinum wire or the tip of a lead pencil and heat it in the bunsen flame. (The pencil or wire should be wetted with hydrochloric acid.) Note the colour of the flame:

Red indicates the presence of calcium.
Green indicates the presence of barium or boron.
Bluish-green indicates the presence of copper.
Bright yellow indicates the presence of sodium.
Lilac indicates the presence of potassium.

The lilac (sometimes called violet) colour of the potassium flame cannot be distinguished by the unaided eye, as it is obscured by the bright yellow of the sodium flame. To separate, the flame should be viewed through a piece of blue glass which cuts off the sodium yellow. (See note *d*.)

5. Take a piece of charcoal and scoop out a shallow pit at one end. Place a portion of the substance in the pit and heat for some minutes in the blow-pipe flame. Note that:

Yellow while hot, white when cold, indicates zinc.
Red globules of metal indicates copper.
White globules of metal indicates lead.

Put a drop or two of cobalt nitrate on to the residue or the charcoal, and heat again.

Green colour indicates the presence of zinc.
Blue colour indicates the presence of aluminium or fusible phosphates.
Pink colour indicates the presence of magnesium.
(See note *e*.)

6. Test the solubility of the substance (that is whether slightly or easily soluble in water or acids) using dilute hydrochloric acid, strong hydrochloric acid, dilute sulphuric acid, nitric acid and aqua regia in the order given should the substance be insoluble in water. (See note *f*.)

7. Examine sand (silica), carbon and sulphur. They are insoluble in the ordinary acids or in water. Ignite carbon and sulphur and note the gases evolved. Fuse some sand with sodium carbonate, extract with water and note that a soluble silicate is formed. (See note *g*.)

NOTES

Note a. The preliminary tests are important because they often allow the student to identify the substance or indicate the class to which it belongs. Success in chemical analysis depends largely on intelligent and methodical use of the process of elimination. The various tests should be applied in the correct order and the process gradually limits down the substance to one class and, finally, allows it to be identified.

Solubility is important as the later tests in Chapters XVIII and XIX are carried out in a solution and these are often affected if the substance can only be dissolved in an acid.

Colour may assist later tests by confirming them. Thus the salts of iron, copper, and other metals are usually coloured, while those of ammonium, potassium, sodium, etc., are nearly always white

Many salts of the heavy metals are insoluble in water, while those of ammonium, potassium and sodium are usually easily soluble. The reaction to litmus may assist in fixing the type of salt. Many are neutral, others such as monocalcic phosphate (found in the manure sold as "super") are acid.

Note b. Care must be taken to ascertain whether the substance is inorganic or organic. Organic bodies ignite when heated, give off carbon dioxide and water, turn black (char) and finally disappear.

Note c. Many organic bodies contain nitrogen and give off ammonia on heating. Others need soda lime to liberate ammonia. They must be distinguished from inorganic salts of ammonia; the latter are crystalline, soluble in water and generally sublime on heating.

Note d. The use of hydrochloric acid is advisable as it reacts with the substance and renders it volatile so that a fair amount is volatilized and the colour can be seen.

The sodium flame (bright yellow) must be considered as an indication only. Sodium is such a general impurity and its flame is so well marked that almost all substances show a yellow flame which may obscure the real flame colour of the salt. If no other metal is identified in the substance or if the flame is very yellow and the colour persists for some time, the presence of a sodium salt may be inferred. Unfortunately, there is no definite test for the metal sodium available for the student as nearly all sodium salts are soluble in water.

Note e. This is really a rough smelting process and beads of the metal can be obtained pure, especially if a little microcosmic salt is added to the salt before heating.

Note f. If the substance is insoluble in water an acid solution must be employed. Some substances are soluble in acids, but reprecipitate

again when the solution is made alkaline with ammonia or soda. Others are decomposed by the acid used and form the soluble salt of the acid. It must be remembered that many tests cannot be employed in an acid solution, as the precipitates are redissolved again.

Aqua regia is a mixture of hydrochloric and nitric acids.

Note g. Many refractory bodies, like sand, react with sodium carbonate on heating and a soluble sodium salt is formed. The metal (if there is one present) is left as the carbonate and can be decomposed with a suitable acid and the usual tests carried out.

XVIII

GENERAL EXAMINATIONS FOR ACIDS

1. If the substance is soluble dissolve in water; but if it is insoluble or partly soluble it will be necessary to fuse with solid sodium carbonate and then to extract with water. (See note *a*.)

(*a*) To the solution obtained add barium chloride. A white precipitate indicates sulphate, phosphate, or carbonate. Add hydrochloric acid to the precipitate; sulphates are insoluble, but phosphates and carbonates dissolve. (See note *b*.)

(*b*) To another portion of the solution add silver nitrate, a white precipitate indicates a chloride or carbonate. Add nitric acid. Chlorides are insoluble but carbonates dissolve. (See note *b*.)

2. Dissolve some of the original substance with a few drops of nitric acid and add some ammonium molybdate. Heat. A yellow precipitate insoluble in acids, soluble in alkalis, indicates phosphates. Repeat, using water alone to dissolve the substance. This will show the presence of *water soluble phosphates*. (See note *c*.)

3. Carbonates give off carbon dioxide when any acid is added to some of the solid or to a water solution.

4. Confirm the presence of chloride found in (1) by (*a*) taking a little of the original solid and dissolving it in dilute nitric acid. Filter if necessary and add silver nitrate to the filtrate. A white precipitate soluble in ammonia indicates chloride. (See note *d*.)

(*b*) Mix with a little manganese dioxide, add sulphuric acid and heat; chlorine will be liberated if a chloride is present.

5. Heat a little of the original solution in a test-tube with some hydrochloric acid. If a carbonate is present carbon dioxide will be given off—the gas turns lime water milky. If the gas evolved smells of rotten eggs, confirm by holding a strip of filter paper moistened with lead acetate over the mouth of the test-tube. If the paper turns brown the presence of a sulphide is indicated. (See note *e*.)

6. Shake some of the original substance with water and filter. To some of the solution in a test-tube add an equal bulk of ferrous sulphate solution and shake well. Pour *strong* sulphuric acid carefully down the side of the test-tube so that it does not mix with the solution, but runs to the bottom. A brown ring where the liquids meet indicates the presence of a nitrate. Confirm by heating a little of the solid with strong sulphuric acid and a fragment of copper in a test-tube. Red fumes given off show the presence of a nitrate. (See note *f*.)

NOTES

Note a. The wet tests for acids are often complicated by the presence of the heavy metals, and if the substance is insoluble it should not be dissolved in hydrochloric or nitric acids, as they are amongst the acids to be tested for in the solution of the base. By fusing with sodium carbonate, double decomposition takes place; carbonates of the bases are formed, most of which are insoluble in water, while the soluble sodium salts of the acids present can be boiled out with water, filtered off and examined. This procedure is unnecessary when special tests are applied, as in the case of phosphates, or when the substance under examination does not contain any of the salts of the heavy metals.

Note b. The addition of barium chloride to a solution brings down sulphates, phosphates and carbonates as barium salts, which are insoluble in water. Of these, barium sulphate is the only one of the three insoluble in hydrochloric acid, so that the addition of hydrochloric acid separates sulphates from the other two.

It may be noted that borates, silicates, oxalates, fluorides, arsenates, iodates, and chromates, as well as silio-fluorides, are also precipitated if present by barium chloride but are not included in the tests given as they are not of general agricultural importance.

The addition of silver nitrate brings down chlorides, carbonates and sulphides as silver salts which are insoluble in water. It may also be noted that the following acids would also be precipitated if present: bromides, bromates, iodides, cyanides, hypochlorites and nitrites. These also are not of general agricultural importance.

It should be noted that if it has been necessary to add sodium carbonate to the solid and fuse, any excess of carbonate left would give the tests for that acid. The original substance should be tested alone for the presence of a carbonate.

Note c. Phosphates are usually tested for separately and a small portion of the original substance should be boiled with nitric acid as most of the phosphates are insoluble in water. The yellow precipitate is ammonium-phospho-molybdate $(NH_4)_6(PO_4)_2(MoO_3)_{24}$ and is soluble in alkalis but insoluble in water.

It is important to discriminate between phosphates soluble in water and those which are insoluble. The monocalcic-phosphate $CaH_4(PO_4)_2$ is the only water soluble phosphate used as a manure and occurs in commercial "superphosphate."

Note d. As carbonates are decomposed by acids, boiling with dilute nitric acid converts all carbonates present to nitrates. The addition of a silver nitrate precipitates chloride as a silver salt.

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

Note e. Lead acetate reacts with sulphuretted hydrogen to form lead sulphide.

$$(CH_3COO)_2Pb + H_2S = 2CH_3COOH + PbS$$

Sulphuretted hydrogen H_2S possesses the characteristic smell of *rotten eggs.*

Note f. Strong sulphuric acid decomposes a nitrate and oxides of nitrogen are given off. NO_2 forms characteristic red fumes.

The action of strong sulphuric acid on a mixture of a nitrate and ferrous sulphate, forming a brown ring where the liquids meet, is due to the fact that the acid decomposes some of the nitrate liberating NO. The NO combines with $FeSO_4$ directly to form the dark brown substance $FeSO_4.NO$. On shaking the test-tube the sulphuric acid and the water become very hot and the $FeSO_4.NO$ is broken up into $FeSO_4$ and NO. The latter is a gas and escapes.

XIX

SCHEME OF ANALYSIS ADAPTED FOR A SOIL OR A PLANT ASH

1. Place a small quantity of the soil or ash in a porcelain dish, add hydrochloric acid, boil well and evaporate to dryness. Allow the dish to cool, moisten with a little hydrochloric acid, add water, boil again and filter off the solution. (See note *a*.)

<table>
<tr>
<td rowspan="3">Insoluble residue. Mix with fusion mixture and fuse on platinum foil. Boil with water and filter. To the filtrate add hydrochloric acid and evaporate to dryness. A white insoluble residue which will not redissolve in water or hydrochloric acid indicates that a silicate was present originally. (See note b.)</td>
<td colspan="3">Filtrate, add a few drops of nitric acid and boil. Cool and add ammonium chloride and ammonia until alkaline. Boil and filter. (See note c.)</td>
</tr>
<tr>
<td rowspan="2">Precipitate (if any) will contain any or all of the following: $Fe(OH)_3 Al(OH)_3 Ca_3(PO_4)_2$ or $MgNH_4PO_4$. Divide the precipitate into several parts. (1) Dissolve in a little nitric acid, add ammonium molybdate and warm: a yellow precipitate indicates a phosphate. (2) Dissolve a little in hydrochloric acid and add potassium ferrocyanide: a deep blue colour indicates presence of iron. (3) Take a good quantity of the precipitate in a test-tube, add sodium hydroxide and boil, cool, dilute and filter. Add ammonium chloride to the filtrate. A white gelatinous precipitate indicates aluminium. (4) Boil another portion with acetic acid and filter if necessary. Add ammonium oxalate to the filtrate: a white precipitate indicates calcium. (5) Take a good quantity of the precipitate and boil it with strong citric acid. Filter if necessary. Add some sodium hydroxide to the filtrate until it is strongly alkaline and stir well with a rod; a white precipitate indicates magnesium. (See note d.)</td>
<td colspan="2">Filtrate, add ammonium oxalate: boil and filter.</td>
</tr>
<tr>
<td>Precipitate (if any). If soluble in hydrochloric acid will be calcium. (See note e.)</td>
<td>Filtrate. Divide into two parts. (1) Cool, add sodium phosphate, and stir. White crystalline precipitate indicates magnesium. (2) Evaporate to dryness and heat until all white fumes have come off. Pick up a piece of the residue on a platinum wire or tip of a lead pencil moistened in hydrochloric acid, and hold in the bunsen flame: (a) an intense yellow flame indicates sodium; (b) lilac flame indicates potassium.
Dissolve the remainder in acetic acid and add sodium cobalti-nitrite: yellow precipitate indicates potassium. (See note f.)</td>
</tr>
</table>

NOTES

Note a. The elements present in soils and other similar bodies are combined in complex salts which are mostly insoluble in water or dilute acids. Small quantities of the various salts slowly become soluble in the soil water and so there may be varying amounts of any element available at any time. The soil thus acts as a reservoir of plant food with considerable amounts potentially available but with only a small proportion actually available at one time. It is important to gain some knowledge of the amount of plant food likely to become available. Hydrochloric acid acts on the soil particles, breaking some of them up so that the bases become soluble as chlorides. A certain amount of silica also goes into solution and as this would come down during the analysis it is got rid of by the evaporation of the hydrochloric acid. This renders the silica insoluble while the chlorides, phosphates, etc., are easily taken up again with dilute hydrochloric acid.

Note b. The fusion mixture reacts with the silicates forming sodium or potassium carbonates which will dissolve in hydrochloric acid. Silicic acid $Si(OH)_4$ will remain in solution if the hydrochloric acid is present in excess. On evaporation it loses water and goes back again to silica SiO_2, insoluble in acids or water. This test is the method used in the preliminary manipulation in para. 1 to get rid of any silicic acid which may have dissolved in the hydrochloric acid on first boiling. The bases present in the soil or ash will go into solution as chlorides.

Note c. Boiling with nitric acid oxidises any ferrous iron there may be present to the ferric state.

Note d. When the solution is made alkaline with ammonia iron and aluminium are precipitated as hydrates while phosphates, which are taken up in acid solutions, will be reprecipitated unchanged. As some of the phosphate is combined with calcium and magnesium, these metals will also be precipitated in this group, although the addition of ammonium chloride and ammonia does not precipitate either metal from a solution.

Note e. The calcium which comes down as calcium oxalate in this group is the calcium from the soluble calcium chloride obtained when the hydrochloric acid acted on the calcium salts of the soil.

Note f. This group includes the metals sodium, potassium and magnesium which cannot be precipitated from a solution by any general group reagent. In testing for sodium by the flame test it must be remembered that very small quantities of sodium will give a yellow flame. The colour must be intense before it can be con-

sidered as indicative of sodium in appreciable quantity. As the bright yellow of the sodium interferes with the observation of the potassium colour the flame should be viewed through a piece of blue glass which cuts off the yellow rays.

Ammonium salts give the same coloured precipitate with sodium cobalti-nitrite as potassium so that it is necessary to get rid of the ammonium salts which have been added during the process of analysis before testing for potassium. All ammonium salts are volatile on heating and so can be removed by evaporation of the solution and ignition of the residue.

General note. If a soil is analysed against a plant ash as a general rule the following results will be obtained:

Soil		Plant
Much	Silica	Little
Much	Iron	Little
Much	Aluminium	Little
Much	Sodium	Little
Variable	Calcium	Little
Variable	Magnesium	Little
Little	Potassium	Much
Little	Phosphates	Much

This shows that the plant requires much of the elements which are naturally present in small quantities in the soil and explains why the application of small quantities of such manures as super, bone, potassium chloride or sulphate may increase the crop considerably.

XX

SCHEME OF ANALYSIS ADAPTED FOR IDENTIFICATION OF MANURES

Table I

Preliminary Examination

I. Examine the appearance of the substance	(1) White crystals slightly tinted with yellow, grey or pink	Salts of sodium, potassium, calcium, magnesium, or ammonia
	(2) Grey, rather damp powder coarsely granular	Superphosphate
	(3) Grey (or brown) dry powder	Ground mineral phosphate
	(4) Dark brown sticky powder not very heavy	Dissolved bones or guano
	(5) Dark heavy dry powder	Basic slag
	(6) Powder sometimes smelling of ammonia	Guano
	(7) White coarse powder with strong organic smell	Bone meal
	(8) Very fine white powder with strong organic smell	Bone flour (See note *a*)
II. Heat a small quantity in a test-tube	(1) Completely volatile, no charring, white sublimate in upper part of tube	Ammonium salt
	(2) White sublimate with non-volatile residue	Ammonium salt in a mixture
	(3) Smell of organic decomposition products, and charring	Bone, guano, or organic refuse manure. (See note *b*)
III. Shake a small quantity with water	(1) Nearly all readily soluble	Sodium nitrate, ammonium sulphate. Chloride or sulphate of potash, kainite
	(2) Large part insoluble. Filter off insoluble part	
	(*a*) Filtrate acid	Superphosphate, dissolved bones, or guano
	(*b*) Filtrate alkaline	Basic slag or lime (See note *c*)
IV. Heat a small quantity with soda lime	Ammonia given off	Ammonium salt, or organic nitrogen. (See note *c*)

V. Heat with a little dilute sulphuric acid	Sulphuretted hydrogen given off	Basic slag
VI. Heat with a little strong sulphuric acid	Hydrofluoric acid given off (which will etch glass)	Ground mineral phosphate

This preliminary table will indicate the class of manure to which the substance belongs: guano and bones differ from mixed manures in that they leave a pure white ash when completely ignited in a crucible.

Table II

Qualitative Examination

1. Boil with water and if only a part dissolves filter. The residue will contain such substances as are insoluble in water. (See note *a.*)

To the filtrate add a few drops of nitric acid and boil. Cool and add ammonium chloride and ammonia until the solution is alkaline. Boil and filter.

<table>
<tr><th>Precipitate</th><th colspan="2">Filtrate</th></tr>
<tr><td rowspan="2">Divide into three parts:
(1) Dissolve in a little nitric acid and add ammonium molybdate solution. Heat. A yellow precipitate indicates a water soluble phosphate. (Superphosphate)
(2) Dissolve in a little hydrochloric acid and add potassium ferrocyanide. Blue precipitate or colour indicates iron. (The presence of iron would mean that the original manure was mineral phosphate, superphosphate or basic slag) (See note d)
(3) Boil with acetic acid and filter. Add ammonium oxalate to the filtrate. A white precipitate indicates calcium. Filter off the precipitate and add ammonia to solution. A white precipitate indicates magnesium (a heavy precipitate would indicate that the manure was probably kainit, a slight precipitate that it was a potash salt)</td><td colspan="2">Add ammonium oxalate and filter</td></tr>
<tr><td>Precipitate indicates calcium (either superphosphate or nitrate of calcium)</td><td>Filtrate. Add sodium phosphate and stir White precipitate indicates magnesium (The presence of much magnesium would show that the manure was kainit)</td></tr>
</table>

Take the insoluble part in (1) and heat it with dilute hydrochloric acid. This will dissolve most of the substances insoluble in water. Filter and examine by Table II.

Table III

Ammonia, potassium and sodium

(*a*) Ammonia will be identified by heating a strong solution of the substance with soda when any ammonia will be driven off. (See note *e*.)

(*b*) Shake some of the original manure up with water and filter, evaporate the filtrate to dryness and ignite to remove any ammonia. Test some of the dry residue with a pencil tip dipped in hydrochloric acid and held in the flame. Lilac flame (viewed through blue glass) indicates potassium. Intense yellow flame indicates sodium.

Dissolve a little of the ammonia free residue with dilute acetic acid, and add sodium cobalti-nitrite. A yellow precipitate indicates potassium.

Table IV

Acids

Test for chlorides, sulphates, carbonates and nitrates. Boil manure with water. Filter if necessary and divide the filtrate into five parts:

(*a*) Add hydrochloric acid—effervescence and CO_2 given off indicates carbonate.

(*b*) To solution add hydrochloric acid and barium chloride—white precipitate indicates a sulphate.

(*c*) Add nitric acid and silver nitrate—a white precipitate indicates a chloride.

(*d*) Mix with equal bulk of ferrous sulphate solution and run strong sulphuric acid down the side of the test-tube—a brown ring where the liquids meet indicates a nitrate.

(*e*) Phosphate will have been identified in Table II. (See note *f*.)

NOTES

Note a. When a manure has to be identified either as a single substance or as a "mixed manure" the work of the analysis is much simplified as the possible range is restricted to the salts and substances usually employed as manures. Artificial manures naturally fall into the following classes:

(1) Comparatively pure salts: nitrate of soda, sulphate of ammonia, chloride of potash, sulphate of potash, "nitrate of lime" and kainit. The last-named is a natural mixture of the chlorides and sulphates of sodium potassium and magnesium.

(2) Natural products: guano, bone and mineral phosphate.

(3) Chemically treated manures: superphosphate, dissolved bones, dissolved guano, bone flour, bone meal.

(4) Manures produced as by-products: basic slag, also shoddy, rape dust and other organic residues.

A preliminary inspection will often give a very good idea of the composition of the mixture, and may also indicate the absence of certain manures. For instance, if all the manure dissolves readily in water or is obviously coarsely crystalline the phosphatic manures cannot possibly be present as none are either coarsely crystalline or entirely soluble in water.

Note b. Most ammonium salts sublime on heating, that is they volatilize and are deposited on the cooler parts of the test-tube. Natural bones and guano contain a considerable amount of organic matter which on heating chars and gives off the strongly smelling products of decomposition. Both bones and guano give a pure white ash on complete ignition.

Note c. Superphosphate is manufactured from mineral phosphate by treatment with sulphuric acid; the equation being:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

The commercial product thus contains two molecules of calcium sulphate to every molecule of pure monocalcic phosphate as well as the impurities originally present in the mineral phosphate. These impurities are largely clay and iron compounds. The pure salt $CaH_4(PO_4)_2$ is soluble in water while the calcium sulphate is only slightly soluble and the impurities practically insoluble. The $CaH_4(PO_4)_2$ is an acid salt and in solution turns blue litmus red. Basic slag is the residue obtained in the process of removing phosphorus from iron. The molecule contains lime loosely combined, and although most of the slag is insoluble the lime gives an alkaline reaction to a solution.

Note d. There would be little or no iron in the water soluble solution but probably a good deal in the residue dissolved in acid.

Note e. Ammonia would be given off from an ammonium salt. Ammonium sulphate is the only ammonium salt used as a manure and is soluble in water, so that a water solution would also give ammonia on boiling with soda.

Organic nitrogen is insoluble in water as a general rule.

Note f. Superphosphate and dissolved bones are the only manures containing a water-soluble phosphate. All the others contain phosphatic salts which are insoluble in water. They are dissolved by hydrochloric acid, but come down in the iron group directly the solution is made alkaline. For this reason it is more convenient to take phosphates in the table of bases.

XXI

ANALYSIS OF PLANTS AND PLANT ASH

1. Test several samples of dry plant substance, as for instance oatmeal, wheat flour, ground hay, pea meal and bean meal, for nitrogen by mixing each of them with soda lime and heating in a dry test-tube. The presence of nitrogen is shown by the evolution of ammonia, NH_3, which can be identified by its smell or, with more certainty, by showing that a bit of red litmus, held in the fumes given off from the tube, turns blue. (See note *a*.)

2. Make a qualitative analysis of plant ash by the tables already given to you on pages 103 to 105. (See note *b*.)

NOTES

Note a. The greatest part of the nitrogen in the plant substance is present in combination with carbon, hydrogen, oxygen and other elements to form complicated organic substances known as proteins. These bodies are entirely decomposed by heating with dry soda lime and the nitrogen is given off, in combination with hydrogen, as ammonia, NH_3.

If litmus paper is used in this experiment, it must only come in contact with the gas evolved in the tube and not with any particles of soda lime which may be adhering to the sides of the tube, since soda lime itself is alkaline and would affect the litmus paper. The amount of nitrogen varies considerably in plants but generally lies between 2 and 6 per cent. of the dry matter.

Note b. The analysis should show that plants contain considerable amounts of potassium and phosphate and smaller amounts of calcium, magnesium, iron, chlorides and sulphates. The amount of ash in plant substances varies considerably but generally lies between 2 and 7 per cent. of the dried material. Two analyses of the ash of plants are given below for reference.

	BARLEY	BEANS
K_2O	20·15	42·49
Na_2O	2·53	1·34
CaO	2·60	4·73
MgO	8·62	7·08
Fe_2O_3	0·97	0·57
P_2O_5	34·87	38·74
SO_3	1·39	2·53
SiO_2	27·64	0·73
Cl	0·93	1·57

XXII

CALCIUM COMPOUNDS

1. *Quick lime.* Weigh out 5 grs. of commercial quick lime into a small beaker. Measure out 50 c.c. of water and take its temperature. Pour the water on to the lime and stir with a thermometer until the temperature ceases to rise. Under these conditions good lime should slake readily and should give out enough heat to raise the temperature of the mixture about 15° C. (See note *a*.)

2. Grind about 10 grs. of commercial quick lime to a very fine powder. Weigh out accurately about 1 gr. of this and transfer it to a 110 c.c. graduated flask. Add 50 c.c. of a 5 per cent. solution of pure phenol and shake vigorously, from time to time, for half an hour. Then make up to the graduation mark with distilled water and filter off 100 c.c. of the solution. To this filtrate add a few drops of methyl orange and titrate with normal hydrochloric acid until a pink tinge is produced. From the amount of normal acid used calculate the amount of calcium in the phenol solution and so the amount of pure calcium oxide in the commercial lime taken. (See note *b*.)

3. Dissolve 1–2 grs. of commercial quick lime in hydrochloric acid, boil and filter. Note the amount of insoluble residue which will give an idea of the amount of insoluble silica and silicates in the sample. Examine the filtrate for metals other than calcium, looking specially for magnesium. (See note *c*.)

4. *Chalk* or *Marl.* Grind about 10 grs. of the sample provided to a fine powder and weigh out accurately from this about 0·1 gr. Transfer this to a bottle fitted with a delivery tube and dropping funnel and add a small quantity of water. Connect the delivery tube with a Lunge nitrometer and run into the bottle, from the dropping funnel, 20 c.c. of strong hydrochloric acid. When the evolution of gas has ceased adjust the nitrometer so that the mercury is level in both limbs and read the volume of gas. This volume, less 20 c.c. (the volume of acid run into the bottle), is the amount of carbon dioxide given off from the chalk taken. Neglect corrections for temperature and barometric pressure and, assuming that 1 gr. of pure calcium carbonate will give 230 c.c. of carbon dioxide, calculate the percentage of pure carbonate in the material taken. (See note *d*.)

5. Dissolve 1–2 grs. of the sample of carbonate provided in dilute hydrochloric acid and note the amount of insoluble residue and magnesium by the method given in Expt. 3 above. (See note *e*.)

6. *Lime requirement of soils.* Weigh out 20 grs. of soil and place in a 500 c.c. bottle. Add 200 c.c. of the prepared calcium bicarbonate solution and shake vigorously for five minutes. Filter. To 100 c.c. of the filtrate add a few drops of methyl orange and titrate with decinormal hydrochloric acid. Titrate 100 c.c. of the original calcium bicarbonate solution in the same way. The difference in the volumes of acid required in the two cases is a measure of the weight of lime absorbed by 10 grs. of soil. Calculate this weight, knowing that 1 c.c. N/10 acid = ·005 gr. $CaCO_3$. From your result calculate the weight of $CaCO_3$ required per acre, assuming that the top nine inches

NOTES

Note a. Quick lime should be reasonably pure calcium oxide, CaO. The heat evolved on adding water is due to a reaction, between the oxide and water, by which calcium hydroxide is formed.

$$CaO + H_2O = Ca(OH)_2$$

The amount of heat evolved will therefore be a measure of the amount of oxide in the lime under examination.

Note b. Calcium oxide and hydroxide dissolve readily in phenol, $C_6H_5.OH$, to give calcium phenolate, $(C_6H_5O)_2Ca$.

$$2C_6H_5OH + CaO = 2(C_6H_5O)_2Ca + H_2O$$

The acid properties of phenol are very weak however and calcium phenolate is as alkaline to methyl orange as the original calcium oxide, while, in addition, the free phenol in the excess used has no reaction on methyl orange. A titration of the solution of calcium phenolate gives therefore the amount of calcium in the solution, the phenolate being decomposed according to the equation

$$(C_6H_5O)_2Ca + 2HCl = CaCl_2 + C_6H_5OH$$

Carbonates, silicates, phosphates, etc., are not attacked and do not dissolve in phenol.

Note c. A good lime should contain very little insoluble matter which is useless for manurial purposes, and for agricultural purposes should contain only a small quantity of magnesium.

Note d. The calcium carbonate in the chalk or marl is decomposed by the acid according to the equation

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

The volume of carbon dioxide evolved is therefore proportional to the amount of carbonate in the original substance and is a measure of its purity.

Note e. See note *c.*

Note f. The bicarbonate solution is made by passing carbon dioxide through milk of lime to saturation when the insoluble calcium carbonate first formed is converted into the soluble bicarbonate

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2$$

XXIII

PHOSPHATIC MANURES

1. Put a little ground bone into a crucible and heat it over a flame. Note that it chars showing that it contains organic matter. Leave it over the flame, stirring it with a glass rod, until all the black is burnt away. The ash should be perfectly white. If it is at all brown or red the bones contain earthy impurities.

2. Dissolve a little of the ash in nitric acid, add ammonium molybdate and warm. A yellow precipitate indicates the presence of phosphate.

3. Shake up a little bone meal with water and filter. Test the clear solution for phosphate with nitric acid and ammonium molybdate. No water-soluble phosphate will be found.

4. Boil up a little bone meal with dilute nitric acid and filter. Test the filtrate with ammonium molybdate for phosphate Note that a large quantity of acid-soluble phosphate is present in bones.

5. Examine guano for organic matter and phosphate exactly as in the case of bones.

6. Repeat the above tests with some ground mineral phosphate. Note that it contains much acid soluble phosphate but no organic matter. Also note that its phosphate is not soluble in water.

7. Place some ground mineral phosphate in a mortar. Moisten it with strong sulphuric acid and a little water. Grind it up to a paste. Scrape it out of the mortar on to a watch glass and keep it until next time.

(See general note.)

NOTE

General note. The natural sources of phosphate for phosphatic manures are:

(*a*) bones,

(*b*) guano,

(*c*) mineral phosphates.

In all three cases the phosphate present is tri-calcium phosphate, $Ca_3(PO_4)_2$, which is insoluble in water. In addition to this main constituent bones contain nitrogenous organic matter, oils and fats and calcium carbonate, together with small quantities of other substances. Guano contains in addition to the phosphate, nitrogenous organic matter (uric acid is frequently the principal nitrogenous compound) though the amount of this varies considerably in different samples. Mineral phosphate contains in addition to calcium phosphate a certain amount of silica, alumina, iron oxide and, in addition, carbonates and fluorides.

The presence of uric acid in guano and fluorides in mineral phosphates will frequently serve to distinguish these substances from bones in analysis

XXIV

MANUFACTURED PHOSPHATIC MANURES

1. Test the preparation made by mixing mineral phosphate with sulphuric acid last time. Note that it now contains much water soluble phosphate.

2. Test commercial superphosphate for water soluble phosphate.

3. Test a little superphosphate with litmus and note that it is strongly acid. (See note *a*.)

4. Test a sample of basic slag for water soluble and acid soluble phosphate.

5. Warm a small quantity of basic slag with dilute sulphuric acid in a test-tube. Hold over the mouth of the test-tube a small piece of filter paper moistened with lead acetate solution. Note that the lead acetate paper is turned brown by the sulphuretted hydrogen evolved.

6. Test a little basic slag with red litmus and note that the litmus is turned blue.

7. Place 10 grs. of basic slag in a standard sieve of 10,000 meshes to the square inch. Shake gently and collect the fine material which comes through on a sheet of paper. Weigh this fine material. At least 8 grs. of the slag should pass through the sieve. (See note *b*.)

NOTES

Note a. Commercial superphosphate is made by acting on mineral phosphate with sulphuric acid. Only sufficient acid is employed to unite with a portion of the calcium of the mineral phosphate with the result that the mixture obtained contains essentially mono-calcium phosphate, $CaH_4(PO_4)_2$, and calcium sulphate, $CaSO_4$. The reaction can be written

$$\underset{\substack{\text{Tri-calcium Phosphate}\\ \text{(Mineral Phosphate)}}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric Acid}}{2H_2SO_4} = \underset{\text{Mono-calcium Phosphate}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium Sulphate}\\ \text{(superphosphate)}}}{2CaSO_4}$$

The mono-calcium phosphate produced is soluble in water whereas the original mineral phosphate was insoluble. Commercial superphosphates will, of course, contain other substances besides calcium sulphate and calcium phosphate, as the original mineral phosphate is never pure tri-calcium phosphate. Commercial samples of superphosphate contain from 12–18 per cent. of P_2O_5. The superphosphate is acid in reaction and should not therefore be used on soils with insufficient lime to neutralise its acidity.

Note b. Basic slag is a by-product in the manufacture of steel and results from the necessity of removing phosphorus from that material. This removal is effected by means of lime with the result that a crude calcium phosphate with an excess of lime is obtained as a by-product. This comes into commerce under the name of basic slag.

Owing to excess of lime present the phosphate in basic slag will be either tri-calcium phosphate or some more basic phosphate; it will not be a water soluble one.

The phosphate present not being water soluble, it is necessary that the material should be very finely ground if the phosphate is to be at all readily available to plants. At least 90 per cent. of the material should pass through the standard sieve. The amount of P_2O_5 present in basic slag varies considerably in different samples but generally lies between 14–23 per cent. The amount of free lime is generally about 5 per cent.

XXV

ESTIMATION OF PHOSPHATE IN MANURES

1. *Superphosphate.* Weigh out 5 grammes of commercial superphosphate and grind it to a cream with a little water. Wash this carefully into a 500 c.c. flask and make up to the mark with distilled water. Shake well and filter through a dry paper into a dry flask. Throw away the first few c.c. which come through, and collect the remainder of the filtrate for analysis. (See note *a*.)

Gravimetric Method I

Take 50 c.c. of the filtered solution which will contain the water soluble phosphate from 0·5 gramme of superphosphate. Add 20 c.c. of bench ammonia and then strong citric acid solution until the precipitate formed on the addition of ammonia redissolves. Pour 30 c.c. of magnesia mixture into a dry filter paper and let it run through into the phosphate solution which should be stirred all the time with a glass rod tipped with rubber. Allow the mixture to stand over night. Filter and wash with dilute ammonia until the washings are free from chlorides (that is, give no cloudiness when tested with NHO_3 and $AgNO_3$). Dry the precipitate in a steam oven and ignite in a porcelain crucible and weigh as $Mg_2P_2O_7$ (magnesium pyrophosphate). Calculate the percentage of P_2O_5 in the original superphosphate. (See note *b*.)

Gravimetric Method II

Take 10 c.c. of the filtered solution obtained as above, add 20 c.c. ammonia solution (sp. gr. 0·9), 100 c.c. water and 25 c.c. strong nitric acid; warm the liquid to 55° C., and add slowly, with constant stirring, 35 c.c. 3 per cent. ammonium molybdate solution which has been warmed to 55° C. Allow to stand until cold. Filter through a Gooch crucible which has been prepared with a well pressed pad of asbestos, dried and weighed. Wash the precipitate several times with 1 per cent. nitric acid, in each case allowing the nitric acid to run through completely before adding the next portion. Place the Gooch crucible inside a nickel crucible, cover with a lid and heat gently until the precipitate becomes blue-black, cool and weigh.

The blue-black precipitate consists of $P_2O_5 24MoO_3$. From the weight of this calculate the percentage of P_2O_5 in the original superphosphate. (See note *c*.)

Volumetric Method

The yellow precipitate obtained as above can be estimated volumetrically as follows: Wash the precipitate on to a filter paper and

wash with a 1 per cent. solution of sodium nitrate until the washings come through neutral to litmus. Transfer the filter paper and precipitate to the beaker used for the precipitation. Add some water and 25 c.c. N/2 NaOH solution until all the yellow precipitate is dissolved. Add 2 c.c. phenol-phthalein solution and titrate with N/2 HCl. The volume of acid required subtracted from the solution of soda added gives the volume of soda neutralised by the yellow precipitate. The yellow precipitate is dissolved according to the equation in note *d*. Calculate amount of P_2O_5 in the superphosphate.

2. *Basic Slag*. Weigh out 5 grammes of commercial basic slag into a beaker containing 20 c.c. strong H_2SO_4. Stir the mixture well and heat on a sand bath until white acid fumes are given off. Cool and wash into a 500 c.c. flask. Shake well, make up to the mark and filter.

Estimate the P_2O_5 in 10 c.c. of the filtered solution by any of the methods given above. (See note *e*.)

NOTES

Note a. The problem is not merely to demonstrate the presence of a phosphate but to estimate the amount present in the given substance. This is called quantitative analysis, and can be carried out either by converting the phosphate into an insoluble body of known composition and weighing this body (gravimetric method) or by finding the volume of a standard solution required to carry out some definite reaction on the given body (volumetric method). It follows, of course, that all weighings or measurements of volume, all transference of material from one vessel to another and all other operations, should be carried out with the greatest accuracy. Of the three methods given the first two are examples of a gravimetric method while the third is a volumetric method.

Note b. The reaction which takes place when the magnesia mixture is added results in the precipitation of magnesium ammonium phosphate, $MgNH_4.PO_4.6H_2O$. This on ignition loses ammonia and water, the filter paper is burnt away leaving only a negligible amount of ash, and magnesium pyrophosphate, $Mg_2P_2O_7$, remains.

$$2MgNH_4PO_4.6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O$$

Note c. The yellow precipitate first obtained consists of the compound, ammonium phospho-molybdate $(NH_4)_6.24MoO_3.(PO_4)_2$.

This on heating loses ammonia and water and leaves the blue-black compound $24MoO_3P_2O_5$ behind. The precipitation of the yellow compound is facilitated by the presence of ammonium nitrate and when precipitation is slow it can often be hastened by the addition of solid ammonium nitrate. The yellow precipitate is soluble in alkalis so that care must be taken that a sufficient excess of nitric acid is present before the addition of the ammonium molybdate.

Note d. The yellow precipitate is decomposed by caustic soda according to the following equation:

$$(NH_4)_6(PO_4)_2 24MoO_3 + 46NaOH$$
$$= 23Na_2MoO_4 + (NH_4)_2MoO_4 + 2(NH_4)_2HPO_4 + 22H_2O$$

The amount of soda used is therefore a measure of the amount of yellow precipitate and so of the percentage of P_2O_5 in the original superphosphate.

Note e. Where basic slag is concerned it is essential to convert the insoluble phosphate contained therein into some soluble form. This is done by the preliminary treatment with sulphuric acid and the estimations can then be carried out as already described.

XXVI

POTASH MANURES

1. Apply the tests for potassium, sodium, calcium, magnesium, chloride and sulphate, to muriate of potash (potassium chloride, KCl), sulphate of potash, K_2SO_4, and kainit. Note the relatively large amounts of substances other than potassium salts in kainit compared with the other two manures. (See note *a*.)

2. Shake up about 5 grammes of each manure with distilled water in a boiling tube. The whole of the manure should dissolve in each case but if there is any sign of undissolved material warm the solution and filter. Examine any residue left on the filter paper, noticing whether it is a sandy or earthy impurity.

3. *Estimation of Potassium in Potassium Chloride.* Place 10 c.c. of a 1 per cent. solution of potassium chloride in a porcelain dish, add 2·5 c.c. of a 20 per cent. solution of perchloric acid and evaporate nearly to dryness on a water bath. Add 20 c.c. of alcohol, stir well with a small glass rod and allow to stand for 10 minutes. Pour off the liquid through counterpoised filter papers and then wash the crystals out of the dish on to the papers with alcohol containing 0·2 per cent. of perchloric acid. Finally well wash the papers and the crystals thereon with 95 per cent. alcohol until the filtrate is no longer acid. Dry in the steam oven and weigh the precipitate as potassium perchlorate, $KClO_4$. Calculate the percentage of potassium, reckoned as K_2O in the original chloride. (See note *b*.)

NOTES

Note a. There are two grades of potassium salts on the market: high grade salts such as the chloride or sulphate of potash, containing about 50 per cent. of potash, reckoned as K_2O, and low grade salts such as kainit, which contain about one-fourth that amount of potash. A high grade salt like potassium chloride will be frequently found to be of more than 80 per cent. purity. The principal impurities are water, sodium chloride, sulphate and perhaps very small quantities of earthy material. Kainit, on the other hand, is a complicated salt, containing as essential constituents large quantities of magnesium and sodium salts in addition to potassium salts.

Note b. The addition of perchloric acid to the potassium chloride solution precipitates the potassium in the form of potassium perchlorate, $KClO_4$.

$$KCl + HClO_4 = KClO_4 + HCl$$

The evaporation, which should be carried on until the mixture is of *a syrupy consistency, ensures that the reaction is complete, and the* crystals, transferred to a filter paper, are washed with acidified and with 95 per cent. alcohol, in both of which they are insoluble, until nothing but pure $KClO_4$ remains on the paper. These crystals are weighed and from the weight the equivalent amount of K_2O can be calculated since $2KClO_4$ will give K_2O, that is 277 grs. $KClO_4$ are equivalent to 94 grs. of K_2O.

XXVII

NITROGENOUS MANURES

1. Mix together a little dried and ground plant substance with soda lime, and heat in a dry test-tube. Test the fumes given off with red litmus paper. Note that it turns blue owing to the presence of ammonia. (See note *a*.)

2. Test several samples of soil by the same method as used for the ground plant substance. Note that the peat soil gives off considerable quantities of ammonia while the other soils give much smaller quantities. (See note *a*.)

3. Examine the given sample of nitrate of soda. Note that it consists of damp white crystals which, in many cases, have a yellowish tinge. Boil about 10 grs. with water in a small beaker and filter. Note if any earthy or sandy impurities remain undissolved and are left on the paper. Test the filtrate for sodium, nitrate, chloride and sulphate. (See note *b*.)

4. Examine the given sample of sulphate of ammonia. Note that it consists of white crystals with a greyish tinge. Using small quantities at a time, test the material for ammonia, sulphate, and sodium

Strongly heat a small quantity of the material in a porcelain crucible over the bunsen flame, in the fume cupboard. Note that the ammonium sulphate volatilizes but there may be a small residue of impurities. (See note *c*.)

5. Place a small quantity of ammonium sulphate in a mortar and just moisten with water. Add a small quantity of lime and grind the two substances up together. Note that ammonia is liberated.

Repeat the experiment using basic slag in the place of lime. (See note *d*.)

6. Test various organic manures, guano, rape dust, hoof and horn, etc., for nitrogen by mixing with soda lime and strongly heating. Ammonia will be evolved in each case and can be identified by its smell or its action on litmus. (See note *a*.)

NOTES

Note a. The organic matter contained in plant substance, soils and the organic refuse manures include many compounds which contain the elements carbon, hydrogen, oxygen and nitrogen. On strongly heating with soda lime these compounds are completely broken down and the nitrogen contained in them is liberated, combined with hydrogen, in the form of ammonia.

Note b. An ordinary sample of air-dried commercial sodium nitrate will frequently contain 94–95 per cent sodium nitrate, 2–3 per cent. water, small quantities of the chlorides and sulphates of sodium, calcium and magnesium, together with slight earthy or sandy impurities. It will be seen from these figures that the tests for sodium and nitrate ought to give very marked results compared with tests for the other bases or acids.

Note c. An ordinary sample of commercial ammonium sulphate will contain about 95 per cent. ammonium sulphate, 2–3 per cent. water and very small quantities of other substances. It should not contain sandy or earthy impurities and should be tested for the possible presence of these by noting whether any portion is insoluble in water. Ammonium sulphate is completely volatile at high temperatures and any residue left after so heating is due to impurities.

Note d. Ammonia salts are decomposed by lime with the liberation of ammonia. In this case the reaction can be represented by the equation

$$(NH_4)_2SO_4 + Ca(OH)_2 = 2NH_3 + CaSO_4 + 2H_2O$$

The free lime contained in basic slag reacts with the ammonium sulphate in the same way. It is clear from these experiments that ammonium sulphate should not, in practice, be mixed with lime or basic slag lest a loss of nitrogen should ensue.

XXVIII

NITROGENOUS MANURES (*cont.*)

1. *Estimation of NH_3 in Ammonium Sulphate.*

(*a*) In pure sample. Weigh out accurately about 1 gr. of the salt and transfer it to a beaker. Add 20 c.c. of normal caustic soda solution and sufficient water for boiling. Boil until ammonia is no longer evolved as shown by testing the steam with litmus paper. Cool, add a small quantity of methyl orange, and titrate the excess of caustic soda with normal sulphuric acid. Subtraction of the volume of normal acid used from the volume of normal caustic soda taken in the first case, will give the volume of soda used to drive off the ammonia from the ammonium sulphate taken. Calculate the amount of ammonia in the ammonium sulphate. (See note *a*.)

(*b*) In impure sample or in mixed manure. Weigh out accurately about 1 gr. of the material and transfer to the distillation apparatus provided. Add about 100 c.c. of distilled water and then slowly, down the side of the flask, about 20 c.c. of strong caustic soda solution. Connect up the apparatus and blow steam through the liquid in the flask, collecting the distillate in a bottle in which has been placed 20 c.c. of normal sulphuric acid. After distilling for some time, disconnect the apparatus, and titrate the normal sulphuric acid in the bottle with normal caustic soda, using methyl orange as an indicator. Subtract the volume of normal soda used from the volume of standard acid first taken. The difference gives the number of c.c. of normal acid neutralised by the ammonia driven over in the steam. This enables the amount of ammonia to be calculated and so the percentage of ammonia in the original manure. (See note *b*.)

NOTES

Note a. In this experiment the ammonium sulphate is decomposed by the caustic soda according to the equation

$$(NH_4)_2SO_4 + 2NaOH = 2NH_3 + Na_2SO_4 + 2H_2O$$

An excess of caustic soda is used, and, after all the ammonia has been driven off, a titration with standard acid shows exactly how much excess of soda was taken. If this excess is known, the difference between these two figures is obviously the volume of normal soda used in decomposing the ammonium sulphate. This enables the amount of ammonia in the ammonium sulphate to be calculated either by use of the above equation or by remembering that 1 c.c. normal soda = ·017 gr. NH_3.

Note b. In this experiment the ammonium sulphate is again decomposed, the reaction being given by the equation in the note above. The ammonia however is not allowed to escape in this case but is carried over in the steam and collected in standard sulphuric acid, with which it combines according to the equation

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

An excess of acid is present in the bottle and the subsequent titration with standard soda enables the amount of this excess to be calculated. If the excess of acid is known, the amount which has combined with the ammonia is also known and either from the above equation or by remembering that 1 c.c. normal acid = ·017 gr. NH_3, the amount of ammonia can be found. Hence the percentage of ammonia in the manure can be calculated.

XXIX

NITROGENOUS MANURES (*cont.*)

1. *Estimation of Total Nitrogen in Organic Manures.* Kjeldahl's method. Take farmyard manure as an example.

Weigh out accurately 1–1·5 grs. of dry and powdered farmyard manure. Transfer this material to a dry hard glass flask and add 20 c.c. of pure strong sulphuric acid, using the acid to wash down into the flask any particles of the manure which may be adhering to the sides. Shake gently until all the material is wet with the acid and then warm carefully until all frothing ceases. Now add about 10 grs. of potassium sulphate and heat more strongly until the liquid becomes colourless. If the dark colour disappears very slowly add a small crystal of copper sulphate, and continue the heating. When colourless, allow the liquid to cool and then carefully dilute with a considerable quantity of water. Transfer the diluted liquid to the distillation apparatus already used for the estimation of ammonia in ammonium sulphate and proceed exactly as for that estimation, using, however, 100 c.c. of strong caustic soda solution in the distillation flask and distilling into 20 c.c. of deci-normal sulphuric acid. Calculate the percentage of ammonia obtained from the dried manure and, assuming that farmyard manure usually contains about 75 per cent. water, convert this percentage to that obtainable from the undried manure. (See note *a*.)

NOTE

Note a. The reaction which goes on during the heating of the manure with strong sulphuric acid cannot be represented by any simple equation. The important part, from the point of view of this estimation, is that the whole of the nitrogen in the manure is obtained in the form of ammonium sulphate, $(NH_4)_2SO_4$. The estimation of the nitrogen becomes therefore a simple estimation of ammonia in ammonium sulphate as described in the previous chapter.

The following points should be noted in connection with the estimation:

(1) The amount of strong sulphuric acid used is not an exact quantity, and can be altered to suit the conditions. The quantity should be kept as small as possible but there should be sufficient to give easy boiling in the flask.

(2) The first heating should be gentle, and should be carefully watched. Many organic substances cause considerable frothing by which some of the contents may be ejected from the flask and the estimation spoilt. This can generally be avoided by careful heating or, at times, by removing the flame altogether for a few minutes.

(3) The potassium sulphate is added merely to raise the boiling point of the liquid and so hasten the decomposition

(4) The amount of strong caustic soda solution added to the reaction liquid in the distillation flask, will vary with the amount of strong sulphuric acid used. There must be sufficient soda to render the distillation liquid alkaline and for this purpose about 5 c.c. of 50 per cent. soda solution for every 1 c.c. of strong sulphuric acid used is generally sufficient.

(5) Deci-normal acid is used instead of normal acid because of the smaller quantities of ammonia being dealt with. It is advisable, however, to add a few drops of methyl orange to the deci-normal acid in the distillation bottle before steaming and to watch that this liquid always keeps its acid reaction. Should it become alkaline owing to more ammonia being obtained than was expected, a further measured quantity, say 20 c.c., of deci-normal acid, must at once be added.

XXX

ORGANIC REFUSE MANURES

1. Examine the refuse manures provided and note their appearance, smell and other obvious characteristics. (See general note.)

2. Treat several of the manures in the following manner. Shake up small quantities of them with distilled water and filter, washing the residue on the filter paper several times. Test the filtrate for nitrate with ferrous sulphate and strong sulphuric acid and also for ammonia by boiling with caustic soda and testing the steam with red litmus paper. Note the absence of nitrates and the rare occurrence of ammonia in these manures. (See note *a*.)

3. Dry the residues left on the filter paper in Expt. 2 in the steam oven. Taking small quantities of these at a time, mix with soda lime in a dry test-tube and heat strongly. Test the gases evolved for ammonia with red litmus paper.

4. Ignite a small quantity of several of these manures in porcelain crucibles until all the organic portion has burnt away. Note that in many cases, the amount of ash is small and therefore there can be very little of manurial mineral substances, such as phosphates or potash, in these manures. Where the mineral residue is sufficient, test this for phosphate and potash.

5. Test rape dust and fish meal for oil by shaking with ether, filtering and evaporating the ether in a porcelain dish on a water bath. Note that an oily residue, which will give a characteristic greasy stain on white paper, remains. (See note *b*.)

NOTES

General note. The organic refuse manures contain a wide variety of substances. Amongst them will be found such materials as rape dust, castor meal, dried blood, various fish manures, leather scrap, hoof and horn, soot, etc. Generally speaking their main value lies in their organic nitrogen content, though a few of them, amongst which soot is especially to be noticed, contain considerable quantities of nitrogen as ammonia. Nitrate is almost invariably absent. A few of them will contain marked quantities of phosphate, this being especially noticeable in the fish and meat meals. Potash is always present in very small quantities. Some typical analyses are given in the appendix.

Note a. In testing for nitrate with these manures it is necessary to remember that soluble organic matter may give a brown ring when strong sulphuric acid is added. It can easily be distinguished from the nitrate ring by the fact that it can be obtained with the sulphuric acid alone without the addition of ferrous sulphate.

Note b. The presence of oil in a refuse manure frequently increases the difficulty of analysis. Where it is present in marked quantities it is advisable to remove it by washing with ether before proceeding with the analysis.

XXXI

FARMYARD MANURE

1. Shake up about 50 grs. of the manure with about 100 c.c. of N/10 hydrochloric acid and allow to stand for some time. Filter off through linen as much as possible of the liquid and evaporate this to dryness on the water bath. Transfer the solid residue to a boiling tube, add sufficient milk of lime to make the solution alkaline and boil. Test the steam coming off with red litmus paper and note that the paper is turned blue by the ammonia evolved. (See note *a*.)

2. Dry the solid matter left on the filter linen in Expt. 1 in the steam oven. Finely grind the dried material, mix a portion of it with soda lime and heat in a dry test-tube. Test the fumes evolved with red litmus paper and note the presence of ammonia. (See note *b*.)

3. Boil some dry powdered farmyard manure with dilute hydrochloric acid for a few minutes. Filter and wash the insoluble residue on the filter paper with hot water. Remove the washed residue to a beaker, add a quantity of dilute ammonia, heat almost to boiling and filter. Acidify the dark coloured filtrate with dilute sulphuric acid and note the brown precipitate of "humic acid." (See note *c*.)

4. Acidify with dilute sulphuric acid some of the dark coloured liquid which has drained from a manure heap. Note that it effervesces and that carbon dioxide is given off and that a brown precipitate of humic acid is obtained. (See note *d*.)

5. Place a few grammes of dry farmyard manure in a porcelain crucible and heat strongly over the bunsen flame until all the black carbonaceous matter has burnt off. Note the whitish ash which remains and test this for phosphate and potash.

NOTES

Note a. Farmyard manure contains nitrogen both in a soluble and insoluble form. In this experiment the soluble forms of nitrogen, largely ammonia salts, are washed out by the hydrochloric acid and on evaporation are left as solid ammonium chloride. This on boiling with lime is decomposed with the liberation of free ammonia

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3$$

Note b. The insoluble nitrogenous compounds in the manure are left behind on the filter cloth. When dried and heated with soda lime these are completely decomposed and the contained nitrogen liberated, combined with hydrogen, in the form of ammonia.

Note c. The organic compounds of an acid nature, known as "humic acid," which are contained in farmyard manure, are present principally in the form of salts, largely those of calcium and ammonium. The boiling with hydrochloric acid removes these bases which then pass through in the first filtering. The "humic acid," now existing as a free acid and insoluble in water, remains behind on the filter paper, mixed with other bodies. Treatment with dilute ammonia dissolves out the humic acid from this mixture and the ammonium humate formed passes through with the filtrate on the second filtering. Acidifying with dilute sulphuric acid breaks up this salt with the formation of ammonium sulphate which remains in solution and the precipitation of the insoluble "humic acid."

Note d. The dark coloured liquid from the manure heap contains, amongst other substances, ammonium carbonate and soluble salts of humic acid. Acidifying with dilute sulphuric acid breaks up these substances, liberating carbon dioxide from the ammonium carbonate and precipitating humic acid.

XXXII

VARIOUS PHYSICAL PROPERTIES OF SOIL

1. *Sand.* Weigh out 50 grs. of sand and pour it into a measuring cylinder. Tap this gently on the bench until the volume of the sand remains constant. Calculate the apparent density.

2 Pour the soil out on to a piece of paper and fill the cylinder with water up to the 50 c.c. mark. Now pour the sand in again and note the volume of sand and water. Calculate the percentage of air-space and the real density.

3. Measure 50 c.c. of sand and pour it into a funnel plugged at the neck with glass wool. Pour 50 c.c. of water on to the sand and collect the water which runs through in a measuring cylinder. (See note *a.*)
Compare:

(*a*) The volume of sand in its ordinary state.
(*b*) The percentages of air-space and particles.
(*c*) The percentage by volume of water retained.

4. *Clay.* Place about 30 c.c. of clay suspension into each of five very clean test-tubes and treat as follows. Add to (1) nothing, (2) 0·5 c.c. very dilute hydrochloric acid, (3) 0·5 c.c. very dilute calcium chloride solution, (4) 0·5 c.c. very dilute sodium chloride solution, and (5) 0·5 c.c. very dilute ammonium chloride solution. Note that the clay flocculates and settles in a short time in tubes (2), (3), (4) and (5) but remains suspended indefinitely in tube (1). (See note *b.*)

5. *Humus.* Boil about 10 grs. of peaty soil with dilute hydrochloric acid. Filter and wash the residue until the washings are free from acid. Test the filtrate for calcium salts. Transfer the lime-free washed soil to a beaker, add ammonia and boil. Filter and note the dark colour of the filtrate. Acidify the solution and note that a dark brown precipitate of "humic acid" separates. (See note *c.*)

6. Put a little dung liquor (the drainage from a manure heap) into a beaker. Note that it is alkaline. Acidify with hydrochloric acid and note the evolution of carbon dioxide and the separation of humic acid. (See note *d.*)

7. *Texture of soils.* Dip a rod into sand. Wet the sand and again dip the rod. Note that in both cases practically no sand clings to the rod. Repeat with wet clay and note that the clay sticks to the rod. Take some recently ignited clay, moisten it and note that only a little clings to the rod. (See note *e.*)

8. Roll out a strip of damp clay and mark its length on a board. Leave the clay to dry and note the contraction.

NOTES

Note a. All soils retain a certain amount of water which varies according to the texture. Sand is composed of particles of hard minerals, mostly quartz, of a comparatively large size, and will only retain a little water. Soils containing much humus or which consist of particles of smaller sizes such as clays are much more retentive.

Note b. "Clay" consists of the smaller particles of a soil and is by convention taken to be all particles which have not sufficient mass to settle through a depth of 8·6 centimetres of water in 86,400 seconds (24 hours). All these particles will have a diameter less than 0·002 millimetre. They are not all about the same size but say from 0·002 millimetre down to almost molecular dimensions. The larger ones will, in course of time, settle through water but the smaller will remain in suspension indefinitely in pure water. Now when a dilute solution of such salts as sodium chloride, ammonium chloride or calcium chloride is added to clay the very small particles flocculate or ball up together and behave as one large mass. In this state they are able to settle through water. "Clay" is carried as "mud" by river water down to the slower-flowing reaches where the larger clay masses have time to settle. Then as the river opens out to the sea the finer, suspended particles come in contact with sea water and flocculation of the clay results.

Note c. The hydrochloric acid decomposes calcium humate and sets free humic acid which settles out in flocks from the acid solution. Organic matter in soils undergoes bacterial action and when partly broken down is known as "humus." "Humic acid" is formed and with the calcium of the soil forms a calcium salt. When the humic acid is boiled with ammonia it goes up into solution and is reprecipitated as humic acid when the solution is acidified.

Note d. Manure heap liquid contains soluble salts of humic acid and also ammonium carbonate formed by the action of bacteria on urea from the urine of cattle. The addition of hydrochloric acid decomposes the humates and the carbonate, so that carbon dioxide is liberated and humic acid precipitated.

Note e. Sand has very little cohesion either wet or dry and therefore makes a light working soil. Clay tends to stick together and forms a heavy working soil especially when such salts as sodium nitrate have been added. Ignition decreases the cohesion of the clay.

XXXIII

RETENTION OF MANURES BY THE SOIL

1. Place 50 grs. of soil in a small flask and add 100 c.c. of a solution containing 0·1 per cent. each of potassium chloride, sodium nitrate and ammonium sulphate. Shake for a few minutes and then filter. Compare the amounts of nitrogen, as nitrate and as ammonia, and of the potash in the filtrate and original solution in the following way.

2. *Nitrogen as nitrate.* Take 1 c.c. of each solution, dilute to 100 c.c. in a flask and take 1 c.c. of each. Place the solutions in two test-tubes of approximately equal diameter and add 3 c.c. strong sulphuric acid to each. Add about 1 c.c. carbazol solution and allow to stand for 5 minutes until the green colour is well developed. Compare the depth of tint by holding the two tubes side by side to the light. Note that the colour is the same in both tubes showing that no nitrate has been retained by the soil. (See note *a.*)

3. *Nitrogen as ammonia.* Measure out 1 c.c. of each solution into 100 c.c. flasks, add 1 c.c. of a 2 per cent. oxalic solution, make up to the mark with tap water, and allow the calcium oxalate precipitate to settle. Pour 50 c.c. of the clear liquids into Nessler cylinders and add 2 c.c. of Nessler solution to each. Note that the brown colour is much more intense in the case of the original solution than in the solution filtered from the soil. This indicates that the soil has retained most of the ammonia. (See note *b.*)

4. *Potash.* Take equal amounts of the two solutions, add a few drops of acetic acid and equal amounts of sodium cobalti-nitrite to each. Note that there is practically no precipitate in the case of the soil solution showing that most of the potash has been retained by the soil. (See note *c.*)

5. *Calcium.* Take equal quantities of each solution and add a few drops of acetic acid and shake up and add equal amounts of ammonium oxalate solution to each. Note that while the original solution contains no calcium, the water which has been in contact with the soil contains a considerable amount. (See note *d.*)

6. Repeat the experiment using a solution made by shaking up 1 gr. of superphosphate of lime with one litre of water and filtering. To compare the amounts of soluble phosphate in the solution before and after shaking up with soil, add to 10 c.c. of each a few drops of nitric acid and 5 c.c. of ammonium molybdate, warm to about 55° C. and note that most of the soluble phosphate has been retained by the soil. (See note *e.*)

NOTES

Note a. Carbazol gives a very delicate reaction with nitrate solutions, hence the need for considerable dilution of the solutions before adding this reagent. If the solutions are used too strong the colour developed is so deep that no comparison can be made.

Note b. The oxalic acid precipitates calcium in the form of calcium oxalate from the solutions and by so doing clarifies them.

The reaction of "Nessler solution" with dilute ammoniacal solutions has been explained in Chapter IX.

Note c. It is usual to remove ammonia before testing for potash with cobalti-nitrite solution but this is not necessary in this case, as the dilution of ammonium salt is so great that no precipitation of ammonium cobalti-nitrite takes place.

Note d. The potassium, sodium and ammonium present in the solution react with the calcium compounds of the soil, replacing a certain amount of the calcium which passes into solution.

Note e. In this experiment the soluble phosphate reacts with the calcium compounds of the soil, particularly the calcium carbonate, with the result that the soluble monocalcic phosphate of the manure is converted into the more basic insoluble phosphates which remain behind in the soil.

XXXIV

RAPID EXAMINATION OF A SOIL

1. The soil to be examined must be air dried, well mixed and passed through a sieve of 3 mm. mesh. Then divide into two portions, one for the mechanical separation and one for the chemical. The latter should be finely ground in a mortar. (See note *a.*)

2. Take the air dried soil (the portion which has not been ground) and weigh out 10 grs. Put the 10 grs. into a beaker which has been prepared by fixing a piece of paper to the side with a mark drawn on it at a height of 7·5 centimetres from the bottom. Add a little ammonia and make up to the 7·5 centimetre mark with distilled water. Stir well with a glass rod fitted with a rubber stopper at the end and allow to stand for 75 seconds. Pour off the liquid leaving the sediment in the beaker and make up to the mark again with water. Repeat the pouring off process until the poured off liquid is clear after standing 75 seconds. Wash the sediment in the beaker into a weighed crucible, dry, ignite and weigh. The result gives the percentage of sand and *gravel in the soil. (See note b.)*

3. Take 10 grs. of the finely ground soil and shake it in a flask with 50 c.c. distilled water for 5 minutes. Filter off some of the solution and place 1 c.c. of it into a test-tube. Add 3 c.c. strong sulphuric acid and mix well by shaking. Cool under the tap and add 1 c.c. of a solution of carbazol in strong sulphuric acid. A green colour will develop on standing, and if well marked, it indicates the presence of nitrates in reasonable amounts and so, by inference, that the soil contains bacteria capable of nitrifying ammonia. (See note *c.*)

4. Place about 5 grs. of the soil in a beaker. Add water and stir until all air bubbles have been removed. Now add about 10 c.c. strong hydrochloric acid. Stir and allow to stand for a few minutes, watching carefully for bubbles of carbon dioxide which indicate the presence of carbonates in the soil. A distinct effervescence shows that at least 1·0 per cent. of carbonates is present which is ample for the normal requirements of a soil. If only a few isolated bubbles appear on the surface, then the percentage is between 1·0 and 0·5 per cent. or near the border line of deficiency of carbonates. If no effervescence can be seen, but a crackling sound of very small bubbles breaking be heard, then the percentage is below 0·5 and the soil needs lime. If no effervescence can be seen or any crackling heard, the soil is practically deficient in carbonates and should be tested for acidity. To do this, lay a strip of blue litmus across a watch glass and pour a small quantity of the fine soil into a heap on it. Moisten

by pouring a very little distilled water round the pile of soil and leave for some time. Wash away the soil and note if the paper has turned red. (See note *d*.)

5. Weigh out 5 grs. of well dried fine soil in a crucible and ignite thoroughly until the soil becomes red in colour Weigh and calculate the loss on ignition. This loss is the residual water and organic matter, and serves as a guide to the nitrogen supply of the soil. (See note *e*.)

6. Take the 5 grs. of ignited soil from (5) and transfer it to a small flask. Add about 15 c.c. strong nitric acid and an equal amount of water. Boil well and filter, allowing all the liquid to run through the filter, and wash with a little dilute nitric acid. Add about 25 c.c. bench ammonia (1 in 3), taking care that the solution remains strongly acid, and 20 c.c. of a 3 per cent. solution of ammonium molybdate.

Heat until the mixture in the beaker is as hot as can be tolerated by the hand, stirring well all the time with a rubber-topped glass rod. Allow the beaker and contents to cool when the yellow precipitate of ammonium-phospho-molybdate will settle out. Pour off the clear liquid and wash the precipitate into a narrow tube, using a little of the poured off liquid to wash the beaker clean. Allow the precipitate to settle again in the tube and compare the amount with a standard tube obtained by the same process from a soil of known composition. This will give a general idea of the amount of phosphorus in the soil under examination. (See note *f*.)

7. Weigh out 5 grs. of soil and place it in a flask with 10 c.c. strong hydrochloric acid and 30 c.c. water. Boil for 5 minutes and filter into a porcelain dish, allowing all the liquid to run through. Wash through with a little water. Evaporate the solution to dryness and ignite the residue over a flame, stirring with a rod until a dry reddish powder is obtained. Cool, add water and boil well. Filter into another small dish again, allowing all the liquid to run through and wash with a little water.

Evaporate nearly to dryness, cool, wash into a narrow test-tube, add a few drops of acetic acid and 5 c.c. of sodium cobalti-nitrite. Allow the precipitate to settle and compare with a similar tube prepared from a soil of known composition. This will give a general idea of the amount of potassium in the soil under examination. (See note *g*.)

NOTES

Note a. In order that a soil may be fertile, it must fulfil the following conditions:

(*a*) It must contain enough calcium carbonate to ensure a permanent neutral reaction.

(*b*) It must contain reasonable amounts of essential plant foods —nitrogen, phosphorus and potassium.

(*c*) It must contain bacteria which can ferment organic matter and others which can nitrify the ammonia produced.

(*d*) It must contain a fair proportion of sand to ensure a certain degree of porosity and freedom in working, as well as clay and silt.

Note b. This process is sufficient to obtain an idea of the amount of the coarser particles present in the soil; but it must be remembered that it is only approximate as the soil aggregations have not been broken up with acid to dissolve out the cementing matter so that the results will tend to be high. The table of soils in the appendix should be consulted and the weights obtained compared with them.

Note c. The carbazol reaction is extremely sensitive, and indicates such small amounts of nitrates as 5 parts in a million. Carbazol is a substance with the formula $(C_6H_4)_2NH$ obtained during the distillation of coal tar and forms a green compound with nitric acid in the presence of sulphuric acid.

If a number of standard solutions of a nitrate are made up the amount of nitrates in a soil solution can be determined quantitatively by matching the depth of colour produced in the soil solution; but for a rough examination the test can be guessed at, especially after a little practice. The main point is that the soil contains nitrifying bacteria.

Note d. The rough separation indicated is quite sufficient to give a good idea of the carbonates in the soil. Anything over 1 per cent. means that there is abundance of carbonates present, while a slight visible effervescence would imply that the amount of carbonates was sufficient, but so low that the continuous application of acid manures might exhaust it dangerously. Anything lower than 0·5 per cent. means that lime is required.

Note e. The residual water in a well dried soil may be taken to average about 2–3 per cent. If the organic matter is high the presence of a reasonable amount of nitrogen may be inferred, and this is a potential supply of nitrates.

Note f. The nitric acid extracts a proportion of the total phosphate

in the soil, especially from the more easily broken down minerals, and this will give a very fair indication of the amount of potentially available phosphorus.

Note g. The hydrochloric acid extracts a proportion of the total potassium and this will give a very good indication of the potash requirements of the soil. Evaporation of the acid extract renders the silica insoluble while the potash is boiled out in the water and precipitated as potassium cobalti-nitrite.

XXXV

MECHANICAL ANALYSIS

1. Take 500 grs. of a well mixed air-dried sample of soil and break it up in a large mortar using a wooden pestle. Transfer to a sieve with a mesh of 3 millimetres (approx. $\frac{1}{8}$ inch) and shake over a sheet of newspaper. Return the residue on the sieve to the mortar, rub up again and repeat the sieving until all the earthy lumps are broken up and only stones with a diameter greater than 3 millimetres are left on the sieve. These stones are washed, dried and weighed and their percentage calculated. The sieved soil is known as "coarse soil sample" and is used for the mechanical separation. Thoroughly mix the soil. Take about 100 grs. of it and grind finely in a small mortar until the whole 100 grs. will pass through a sieve with a mesh of 1 millimetre and thoroughly mix again. This is the "fine sample" and is used for determination of water and organic matter. (See note *a*.)

2. Weigh out 10 grs. of the "coarse soil" and place it in a beaker with 100 c.c. N/5 hydrochloric acid. Allow the soil to stand for one hour, stirring occasionally. (See note *b*.)

3. Pour the soil on to a filter paper, taking care that all particles of soil are washed out of the beaker, and wash with distilled water until the soil and filtrate are free from acid. (See note *c*.)

4. Spread the filter paper containing the washed soil on a clock glass, taking care that none of the soil is lost, and wash on to a small sieve with a mesh of 0·25 millimetre ($\frac{1}{100}$ inch). This sieve should rest in the mouth of a 300 c.c. beaker, and should be thoroughly wetted before the soil is washed into it. A strip of paper must be gummed on the side of the beaker and a pencil mark made at a height of 7·5 centimetres from the bottom. Rub the soil on the sieve with the forefinger, adding small quantities of water from a wash bottle, until the washings run through quite clear. Dry the particles, with the sieve, in the water oven and then ignite them in a crucible to burn away organic matter. Turn the particles on to a sieve with a mesh 1 millimetre in diameter and collect that portion which passes through, on a sheet of paper. Weigh both these and the larger particles on the sieve. The first fraction so separated contains fragments varying between 3 and 1 millimetres and is left on the 1 millimetre sieve. It is known as "fine gravel." The smaller particles between 1 and 0·25 millimetre pass through the 1 millimetre sieve and are known as "coarse sand."

Express the result as percentages. (See note *d*.)

5. Take the muddy washings in the beaker. These will include all particles having a diameter of less than 0·25 millimetre. Fill up the beaker with water until the level of the liquid is in line with the pencil mark on the paper strip. Add a few drops of ammonia solution. Stir well with a glass rod, tipped with a rubber bung, and withdraw it after making two or three vertical movements so that the liquid is not left with a circular swirl. Allow it to stand for 75 seconds and then pour off into a large beaker, quickly and steadily without shaking, so that the heavier particles which have settled to the bottom are left in the beaker. Repeat this several times until the liquid pours off clear after standing 75 seconds. Transfer the fraction left behind to a crucible, dry and weigh. This fraction contains all particles varying in size between 0·25 and 0·04 millimetre in diameter and is known as "fine sand." Express the result as percentage. (See note *e*.)

6. Take all the poured off muddy washings in the large beaker and add about 50 c.c. ammonia solution. Stir well, add enough hydrochloric acid to make the mixture faintly acid, and leave for two days.

Decant off the clear liquid as far as possible and filter off the remainder. Dry the filter paper, leaving it in the funnel. Then roll it up, place in a crucible and ignite. This fraction contains all the soil particles with a diameter less than 0·04 millimetre. It is known as "silt and clay." Express the result as percentage. (See note *f*.)

7. Take the "fine sample" and weigh out 10 grs. in a crucible. Place in a water oven at 100° C. until the crucible and soil are at constant weight, or for 24 hours. Express the loss, which is residual water, as percentage.

8. Take the crucible and dry soil from experiment (7) and ignite it strongly over a Teclu burner for some time, stirring occasionally with a stout copper wire until the soil becomes of a reddish colour. Cool and weigh. Express the loss, which is organic matter, as a percentage. (See note *g*.)

NOTES

Note a. It is exceedingly important to get a fair sample of the soil of any field or area. The proper method is to take at least six borings to a depth of 9 inches with a 2 inch cylinder and mix them together. Such a sample would weigh about 10 lb. Nine inches is the average depth of "soil" in a field under cultivation and the second 9 inches in depth is also generally taken at the same time. This is known as the sub-soil. Stones vary very much in size. Only those which will pass into the barrel of the sampler will be included. If the soil is very stony it may be necessary to use a spade and take six spadefuls of the soil. These spadefuls are well mixed and about 10 lb. of the mixture taken. The soil is then dried at about 30° C. for some days.

Note b. Soil particles are often cemented together with calcium carbonate or iron oxide. The dilute hydrochloric acid breaks this cement up and allows the particles to fall apart. N/5 hydrochloric acid (0·75 per cent.) is not strong enough to attack the ordinary soil minerals. If the soil contains much calcium carbonate further lots of acid or a few drops of strong hydrochloric acid should be added until all effervescence has ceased.

Note c. The soil must be washed free from acid, otherwise organic matter would be precipitated bringing with it particles of soil which would be included with the next fraction instead of being poured off.

Note d. It is advisable to wet the sieve as otherwise the liquid does not run through and is apt to pour over the rim and spill on to the bench.

The size of the different particles in each fraction is purely arbitrary and is the generally accepted standard for Great Britain.

Note e. The smaller sized particles are too small for separation by a sieve so the method of sedimentation is adopted. Particles of a certain size fall through water at about the same rate, the heavier ones settling out first. By allowing a definite time similarly sized particles will always fall to the bottom of a constant depth of water together. Smaller particles which happen to be suspended near the bottom when the stirring stops will also settle as they have a less distance to fall, but by repeatedly stirring and pouring off the liquid all the small particles will be finally caught while only the heavier ones will always settle out no matter at which height they are started.

Note f. The addition of ammonia and hydrochloric acid causes the clay particles which are very minute to flocculate and form comparatively large masses. These will settle out as if they were one large

particle and on standing the whole of the silt and clay falls to the bottom of the beaker, leaving a clear liquid which can be nearly all decanted off. The remainder can be filtered off in a few minutes. The ash of the ignited filter paper is negligible in amount. A certain amount of ammonium chloride formed by the hydrochloric acid and ammonia remains with the damp soil and paper but volatilizes on ignition.

Note g. The "dry" soil always contains a certain amount of water which is lost on ignition of the various fractions but the amount must be determined to make the total, when the different fractions are added together, agree with the weight of soil originally taken. Organic matter which is always present in soils must also be determined and added to the total.

It will be found that the total of the fractions, with the moisture and organic matter, never adds up exactly to the original weighing. This is because a certain amount of the soil is dissolved by the water during separation and also because any carbonate such as chalk originally present will also be dissolved out. To complete a mechanical analysis the amount of carbonate present should be ascertained and also added to the total. During ignition of the organic matter any chalk will be converted into lime and, if the soil is very rich in chalk, a correction of $\frac{44}{100}$ of the chalk should be allowed, this being the percentage of CO_2 lost.

GENERAL PHYSICS

XXXVI

PROPERTIES OF GASES

1. Take the large round-bottomed flask provided and see that the rubber bung with which it is fitted is tight. Connect the end of the rubber tube with the filter pump. Turn on the pump and allow it to run for several minutes. Then close the screw and clip before removing the flask or turning off the pump. Disconnect the pump and turn it off. Weigh the flask as accurately as possible. Note the weight and then open the clip. Weigh again and note that the weight has increased. (See note *a*.)

2. Repeat, using the same apparatus, and then fill the flask with carbon dioxide gas by downward displacement. Replace the bung and weigh again. Note that the weight has increased. (See note *b*.)

3. Counterpoise a beaker on the balance and prepare a gas cylinder full of carbon dioxide. Pour the gas into the beaker and note that the balance pan is depressed owing to the increased weight.

4. Take the glass tube provided, which is sealed at one end, and fill it completely with mercury. Remove any air bubbles which may adhere to the side of the tube by gently tapping the glass: close the end of the tube with the finger and invert in a small dish of mercury, taking great care that no bubbles of air are allowed to enter. Clamp the tube in its upright position and note that the mercury comes to rest at a definite height above the level of the mercury in the dish. Measure the height and record it in your note book. Release the tube from the clamp and incline it at various angles to the vertical. Note that the *vertical* height of the mercury in the tube above the mercury in the dish is always the same, although varying lengths of the tube will be occupied by it. When the vertical height of the tube is less than the figure obtained above note that the mercury completely fills it, running up with a metallic click. (See note *c*.)

5. Return the tube to the vertical position and clamp it firmly. With a piece of glass tube blow a few bubbles of air into the barometer tube and note that the mercury column is depressed, coming to rest again at a lower level.

6. Empty out the mercury carefully and repeat Expt. 4, using water instead of mercury. Note that the water completely fills the tube.

NOTES

Note a. This experiment illustrates the fact that air has weight. The flask is, at the beginning, full of air. The water pump removes the greater part of this and the first weighing is done on a flask almost free from air. On opening the clip air fills the flask again and the weight is thereby increased.

Note b. The difference in weight in this case is caused by the fact that the carbon dioxide is much heavier than air. When the air is replaced by carbon dioxide an increase in weight is observed.

Note c. It has been pointed out in note *a* that air has weight. Owing to this weight the atmosphere will exert a pressure on all surfaces. In Expt. 4 the mercury in the dish is subject to the pressure of the atmosphere while the mercury column in the tube is not subject to this pressure owing to the end of the tube being sealed. The mercury is therefore held up in the tube to such a height that the weight of the column of mercury is equal to the weight of the atmosphere. Since this weight of the atmosphere may vary from day to day, the height of the mercury column will vary correspondingly. This arrangement of a mercury column is known as a "barometer."

Since the pressure exerted by a column of liquid in a barometer tube depends on the vertical height of its surface above the surface of the liquid in the dish and not on the total amount in the tube, the inclining of the tube in Expt. 4 results in the same vertical height being always maintained.

If a bubble of air is introduced into the barometer tube, this air immediately exerts a pressure on the surface of the mercury. This pressure counterbalances a portion of the atmospheric pressure and the mercury column is correspondingly depressed.

If the mercury in the tube is replaced by any other lighter liquid, the same conditions obtain, but the height of the column will be increased as a greater height is required to balance the air pressure. As water is about one-thirteenth as heavy as mercury, the column of water in a water barometer would be thirteen times as high as the mercury in Expt. 4.

XXXVII

PROPERTIES OF GASES (*cont.*)

1. You are provided with a U tube with limbs of unequal length. The shorter is sealed at the end while the long limb is open to the air. Run a small quantity of mercury into the bend of the U tube, thereby trapping a certain amount of air in the shorter limb, arranging, as far as possible, that the mercury stands at the same height in both limbs and is sufficient in quantity to reach the straight portion of each.

Note the length of the enclosed column of air, the difference in level of the mercury in the two limbs and obtain the barometer reading for the day.

Now add mercury carefully down the open limb of the tube until sufficient has been added to cause a difference in level of a few inches. Again note the length of the enclosed air column and the difference in level of the mercury in the two limbs.

Repeat, adding more mercury and taking readings at convenient stages until the long limb of the U tube is full. Mark off five columns in your note book heading them (1) Volume, (2) Difference in level, (3) Height of barometer, (4) Total pressure, (5) Volume × pressure. Enter in the first column the measured lengths of enclosed air, in column 2 the difference in levels of the mercury in the two limbs, measured in millimetres, in column 3 the height of the barometer in millimetres, in column 4 the sum of the values in columns 2 and 3 and in column 5 the products obtained by multiplying together the values in columns 1 and 4.

Note that the values obtained in column 5 are practically constant. (See note *a*.)

2. Fit a flask of from 250–500 c.c. capacity with a well-fitting cork through which passes a straight piece of tubing about 2 feet long. Clamp this flask in an inverted position in such a way that the tubing dips into a beaker full of water. Warm the flask by placing the hand on it and notice that the air inside the flask expands and that bubbles escape through the water in the beaker. Remove the hand from the flask and notice that the water rises up the tube to take the place of the escaped air. (See note *b*.)

When the water has become steady in the tube repeat the experiment, noting that alternate warming and cooling of the flask results in the expansion and contraction of the enclosed air.

3. Fit the flask used in Expt. 2 with a well-fitting cork and a leading tube bent as for the collection of gases over water. Note the point to which the cork fits into the neck of the flask and measure

the volume of the flask to this point by filling with water and pouring the water into a graduated cylinder. Now fit up the apparatus so that the flask is surrounded by a water bath and the leading tube passes into a trough of water, a graduated tube full of water being inverted over the end of the leading tube. The flask should be clamped so that it stands as deeply in the water bath as possible.

Note the temperature of the water in the water bath and then heat up the bath until the water boils. The air in the flask will expand and some will be driven over into the graduated tube. When the expansion is complete, measure the amount of gas which has come over into the graduated tube, arranging that the water stands at the same level inside and outside the tube before taking a reading. Knowing the initial and final temperatures of the water bath, the volume of air contained in the flask and the amount passing over into the graduated cylinder, calculate what fraction of the original volume the gas expands for every one degree Centigrade the temperature rises. (See note *c*.)

NOTES

Note a. The experiment illustrates the effect of pressure on a gas, in this case, air. This effect is summarised in what is known as Boyle's Law, which can be stated as follows: "The volume of any gas, at a constant temperature, varies inversely as the pressure to which it is subjected." That is, if the pressure be doubled the volume is halved, if the pressure be halved the volume is doubled, etc.

The statement can be put shortly in symbols in the following manner.

Let p = pressure, v = volume and K be a constant.

Then v varies as $\frac{1}{p}$.

That is $v = K\frac{1}{p}$.

or $pv = K$;

that is, the pressure multiplied by the volume gives a constant quantity.

Note b. This experiment merely illustrates qualitatively the fact that gases expand on heating and contract on cooling.

Note c. Expt. 3 illustrates in a very rough manner what is known as Charles's Law. This can be stated as follows: "The volume of any gas, at constant pressure, increases by $\frac{1}{273}$ of its original volume for every degree Centigrade the temperature rises."

This can be stated algebraically in the following way. If v = original volume, v_1 = volume at some higher temperature and t = number of degrees Centigrade the temperature has risen, then

$$v_1 = v\left(1 + \frac{vt}{273}\right).$$

XXXVIII

DENSITY, SPECIFIC GRAVITY. (SOLIDS)

1. A solid of regular shape. Take as an example a rectangular block of wood. Measure the length, breadth and thickness of the block in centimetres and fractions of a centimetre and by multiplying these three dimensions together find the cubic content of the block in cubic centimetres. Then weigh the block and note its weight in grammes and fractions of a gramme. Knowing the volume and the weight, calculate the density of the wood. (See general note.)

2. A solid of irregular shape. Use the piece of stone provided. Weigh the stone and note its weight in grammes. Then fill a graduated cylinder up to a definite mark with water and drop the stone into the water. See that no air bubbles adhere to, or are caught under, the stone. Now read the rise in the water in the cylinder. This will correspond to the volume of the stone in cubic centimetres. Knowing the weight and the volume calculate the density. (See general note.)

3. A solid of irregular shape and lighter than water. Use the piece of paraffin wax provided. Weigh the wax and note the weight in grammes. Into a graduated cylinder with water up to a definite mark drop a small stone or piece of metal. Note the rise in level of the water and record this as the volume of the stone. Take the stone out of the water and tie the paraffin wax provided to it, with a thin piece of cotton. Now drop stone and wax into the water in the cylinder and again note the rise in level. The difference between the rise this time and when the stone alone is used is evidently the volume of the wax. Knowing the volume and weight of the wax calculate its density. (See general note.)

4. By weighing in air and water. Weigh the given piece of metal or stone in air and note its weight in grammes. Then suspending it by a piece of fine cotton weigh it in water, using the apparatus provided. Care should be taken that no air bubbles adhere to the cotton or the metal when this weighing in water is carried out. Knowing the weight in air and the weight in water, calculate the specific gravity of the material used. (See note *a*.)

5. Apparent and true density of a material occurring in small particles. Use sand as the material.

Apparent density. Weigh accurately between 20 and 30 grammes of sand and note the weight in grammes. Tip the sand into a dry graduated cylinder and tap down the sand until the surface is level. Read off

on the cylinder the volume of the sand in cubic centimetres. Knowing the weight and the volume, calculate the apparent density.

True density. Again weigh out accurately between 20 and 30 grammes of sand and note the weight in grammes. Then tip the sand into a graduated cylinder containing water up to a definite mark. Note the rise in the level of the water. This will give the combined volume of all the sand particles. Knowing this volume and the previously ascertained weight, calculate the true density of the sand. (See note *b*.)

6. Find the percentage of pore space in a given sample of sand. In a graduated cylinder measure out 30–40 c.c. of sand and note the volume accurately. Take out the sand from the cylinder and fill it up to a definite mark with water. Again tip the sand into the cylinder and note the rise in the level of the water. From these two measurements calculate the percentage of pore space in the sand. (See note *c*.)

NOTES

General note. In carrying out these experiments attention should be paid to the definitions of density and specific gravity. Density is the relation between the weight and the volume of a substance. That is,

$$\text{Density} = \frac{\text{Weight of substance}}{\text{Volume of substance}}.$$

Specific gravity is the ratio between the weight of a given substance and the weight of an equal volume of water. That is,

$$\text{Specific gravity} = \frac{\text{Weight of substance}}{\text{Weight of an equal volume of water}}.$$

If grammes and cubic centimetres are the units used, the two fractions shown above will be identical since 1 c.c. of water weighs 1 gr., that is the density and specific gravity of a substance will be represented by the same figure.

Expts. 1–3 are merely examples of how the weight and volume, and hence the density, of a given substance can be found. In Expt. 3 the substance whose density has to be found is lighter than water and consequently it must be made to sink by attaching to it a piece of denser material.

Note a. When a substance is weighed in air and then weighed in water, it suffers an apparent loss of weight. This loss in weight can be shown to be the weight of a volume of water equal in volume to the submerged substance. But this is one quantity required for the determination of the specific gravity. If therefore we represent the weight of the substance in air by W and the weight in water by W_1, the loss of weight in water will be represented by $W - W_1$ and the specific gravity will be given by

$$\frac{W}{W - W_1}.$$

Note b. The two quantities required for the determination of the density are the weight and the volume. In the case of a substance occurring in small particles like sand, the volume measured may be either the volume of the particles and all the small interstices between the grains or it may be the volume of the grains alone. In the first part of this experiment where the volume is measured in a dry cylinder, both the volume of the grains and of the interstices is taken and the density calculated when this volume is used is called the "apparent density."

In the second case, where the sand is tipped into water, the volume of the particles alone is found, without the volume of the interstices,

and the density calculated using this volume is known as the "true density."

Note c. In this experiment the combined volume of the actual grains of sand and the pores between the grains is found in the dry cylinder. On tipping into water the volume of the grains alone is found. The difference is evidently the volume of the pores. A simple calculation then gives the number of cubic centimetres of pore space in 100 c.c. of sand.

XXXIX

DENSITY, SPECIFIC GRAVITY. (LIQUIDS)

1. *By direct weighing.* Use alcohol as the liquid whose specific gravity is to be determined.

Dry and weigh the small beaker provided and note this weight as W. Run into the beaker 10 c.c. of distilled water, measuring this accurately either with a pipette or a burette. Again weigh and note the new weight, W_1. Pour out the water, dry the beaker and run in 10 c.c. of alcohol. Again weigh and note this weight as W_2. The weight of the water is the difference between W_1 and W, that is, $W_1 - W$. The weight of the alcohol is $W_2 - W$. The specific gravity of the alcohol is therefore $\frac{W_2 - W}{W_1 - W}$. (See note *a*.)

2. *By Hare's Apparatus.* An apparatus is provided consisting of a U tube with long limbs and with a short tube sealed on at the end of the U. This small piece of tube is fitted with a short length of rubber tubing provided with a clip. The apparatus is inverted so that each limb dips into a beaker and is clamped in this position. If the specific gravity of alcohol is to be determined this liquid is introduced into one beaker and distilled water into the other. The clip on the rubber tube is loosened and, by sucking, the liquids are drawn up in the tubes until they stand at about three-quarters of the height of the tubes. Close the clip and the liquids will remain at the height to which they have been drawn. Measure the distance from the level of the water in the beaker to the level of the water in the tube and call this L. Also measure the distance from the level of the alcohol in the beaker to the level in the tube and call this L_1. Then the specific gravity of the alcohol is L divided by L_1. (See note *b*.)

3. *By the U tube method.* Use milk as the liquid whose specific gravity is to be determined. Clamp the U tube provided in an upright position and introduce into the bend of the tube, an inch or so up each limb, a quantity of coloured chloroform. Now to one limb add water and to the other milk, until these liquids stand almost to the top of the U tube. (The water and milk should be added to their respective limbs alternately and in small quantities at a time or they will probably get round the bend of the tube and so into the wrong limb.) Towards the end of the addition of the two liquids add more of one or the other until the chloroform level in both limbs is the same. When this is the case measure the distance from the chloroform to the top level of the water and call this L. Then measure the distance from the chloroform to the top level of the milk and call this L_1. Then the specific gravity of the milk is found by dividing L by L_1. (See note *c*.)

4. *By the hydrometer.* With the set of hydrometers provided find the specific gravity of the given solution of alcohol and of milk.

NOTES

Note a. The meaning of the term specific gravity should be constantly borne in mind during the experiments. It can be defined, as the ratio of the weight of a given substance, to the weight of an equal volume of water. In Expt. 1 equal volumes of water and alcohol are weighed and the specific gravity of the alcohol is obtained by dividing the weight of the alcohol by the weight of the water. It is, of course, necessary to subtract, in each case, the weight of the beaker from the total as registered by the balance before the weights of the water and alcohol can be obtained.

Note b. In this experiment the columns of water and alcohol in the two limbs of the apparatus are supported by the pressure of the atmosphere on the surface of the liquids in the beakers. Since this will be the same in both beakers, it follows that the column of water is of the same weight as the column of alcohol. Measurement of the length of the columns will give a measure of their respective weights and therefore the specific gravity can be found by dividing the length of one column by the length of the other. There is sometimes some confusion as to which length should be made the divisor. The student can easily argue this out for himself in the following way. The column of alcohol is longer than the column of water. Therefore the alcohol must be lighter than water since it takes more of it to counterbalance a certain atmospheric pressure. That is, the specific gravity of alcohol is less than that of water and must be represented by some figure less than unity. In dividing the length of one column into the length of the other the smaller quantity must therefore be divided by the larger.

Note c. The argument set out in note *b* should, in this experiment also, enable the student to decide which of the measured lengths should be made the divisor. It should be remembered that the chloroform takes no part in the experiment except to separate the two liquids in the limbs of the tube. It could be replaced by any other liquid which does not happen to be miscible with the two liquids used.

NOTES

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Note b. In this experiment the columns of water and alcohol in the two limbs of the apparatus are supported by the pressure of the atmosphere on the surface of the liquids in the beakers. Since this will be the same in both beakers, it follows that the column of water is of the same weight as the column of alcohol. Measurement of the length of the columns will give a measure of their respective weights and therefore the specific gravity can be found by dividing the length of one column by the length of the other. There is sometimes some confusion as to which length should be made the divisor. The student can easily argue this out for himself in the following way. The column of alcohol is longer than the column of water. Therefore the alcohol must be lighter than water since it takes more of it to counterbalance a certain atmospheric pressure. That is, the specific gravity of alcohol is less than that of water and must be represented by some figure less than unity. In dividing the length of one column into the length of the other the smaller quantity must therefore be divided by the larger.

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XL

THERMOMETERS, MELTING AND BOILING POINTS

1. Check the accuracy of the zero point of the given thermometer in the following manner. Crush up some ice into small pieces about the size of beans and put the crushed ice in a funnel stood in a beaker. Place the thermometer in the ice with the bulb about half way down the funnel. Note that the thermometer immediately falls and comes to rest, if the thermometer is accurately graduated, at the zero point. If the thermometer does not become stationary at the zero point, but at some other point, note the degree of inaccuracy. Try this experiment for both a Centigrade and a Fahrenheit thermometer and note what figure is registered on the Fahrenheit thermometer when the Centigrade thermometer stands at zero. (See general note.)

2. Fit up a small flask with a cork, in the side of which a slit has been cut and through a hole in which a Centigrade thermometer passes. Place water to the depth of about an inch in the flask and replace the cork with its thermometer, arranging that the latter passes down to within about an inch of the water. Heat the flask on a wire gauze over a bunsen flame until the water boils vigorously and then read the thermometer, noting the temperature registered. If this temperature is not exactly 100° note the amount of inaccuracy. Repeat the experiment using a Fahrenheit thermometer and note the boiling point of water as registered on this. (See general note.)

3. Suspend a Centigrade and a Fahrenheit thermometer side by side in a beaker of water and read the temperature registered on both. Gradually warm up the water with a small bunsen flame, stirring constantly, and at approximately regular intervals of about 10° Centigrade, take simultaneous readings on the two thermometers, noting these pairs of readings at the time. When a series of seven or eight pairs of readings has been taken, plot the Centigrade readings against the Fahrenheit readings on squared paper and show the result in the form of a curve. (See general note.)

4. Find the melting point of paraffin wax in the following manner. Take a length of about 2–3 inches of the fine capillary tube provided and just dip one end of it into molten paraffin wax. A small quantity of the wax will run up into the tube and the tube is then withdrawn and the small portion in the capillary tube is allowed to cool, when the wax will solidify. The small capillary tube is now attached to a thermometer by merely wetting both tube and thermometer and placing them in contact. They will be found to adhere to one another

quite easily without any other means of attachment. The capillary tube should be at such a position on the thermometer that the paraffin wax is alongside the bulb. The thermometer with its attached tube is now suspended in a beaker of water and the water very slowly heated until the paraffin melts. This point is well marked by the paraffin suddenly rising in the capillary tube. Note the temperature at this point as the melting point of the wax.

5. In the small distillation apparatus provided place a quantity of alcohol. Heat gently over a bunsen flame and when the alcohol is distilling freely, read the temperature registered by the thermometer. Note this as the boiling point of alcohol.

NOTE

General note. The two fixed points from which thermometers are graduated are the melting point of ice and the boiling point of water. The melting point of ice is marked as 0° on the Centigrade thermometer and as 32° on the Fahrenheit thermometer. The boiling point of water is marked as 100° on the Centigrade thermometer and as 212° on the Fahrenheit thermometer. There are therefore 100° between the two fixed points on the Centigrade thermometer and 180° between the same two points on the Fahrenheit thermometer. That is 100° Centigrade are equivalent to 180° Fahrenheit, or 5° Centigrade are equivalent to 9° Fahrenheit. Bearing these facts in mind, the conversion of a reading on one scale to the corresponding reading on the other is easy. It can be put shortly thus:

Centigrade to Fahrenheit. Multiply by nine and divide by five and then add thirty-two.

Fahrenheit to Centigrade. Subtract thirty-two and then multiply by five and divide by nine.

XLI

SPECIFIC HEAT

1. Take two beakers of about 300 c.c. capacity. Weigh out into each 100 grs. of water. Keeping one at the laboratory temperature, raise the temperature of the other to 40° C. by warming over the bunsen flame.

Now take the temperature of the colder water accurately with a thermometer and, having made a note of this temperature, pour the warm water into the cold water. Stir well with a thermometer and note the temperature of the mixture. Now repeat the experiment but this time weigh out 100 grs. of alcohol into one beaker while 100 grs. of water are weighed out into the other beaker. Again raise the temperature of the water to 40° C. and pour this warm water into the cold alcohol, having first read the temperature of the alcohol accurately. Having stirred the mixture well note in this case also the final temperature.

Compare the rise of temperature in the two experiments. (See note *a.*)

2. To find the specific heat of a piece of metal. Weigh the small calorimeter provided and weigh out accurately into it about 100 grs. of water and note the temperature (T). Stand the calorimeter on a cork mat on the bench. Weigh the small piece of metal provided. Tie a piece of cotton round it and by means of the cotton lower the metal into a beaker containing cold water, leaving the cotton hanging over the side of the beaker.

Now heat up the beaker containing the water and metal until the water boils (100° C.). When the water has been boiling for a few minutes lift out the metal by means of the attached cotton, very rapidly remove any drops of water attached to it by touching with filter paper and drop it quickly into the water in the calorimeter. Stir the water in the calorimeter with a thermometer and, as the temperature rises, note the highest temperature recorded, T_1. Knowing the weight of the calorimeter, the weight of the water contained therein, the weight of the metal heated to 100° C., the initial and final temperatures of the water in the calorimeter, and the specific heat of the calorimeter material, calculate the specific heat of the given metal.

You are given the specific heat of the calorimeter material. (See note *b.*)

3. Repeat Expt. 2 but, in this case, find the specific heat of sand instead of that of a piece of metal. The experiment is carried out as

described above, except that the sand obviously cannot be heated in quite the same way as the metal.

The method adopted for heating the sand is to place the weighed quantity in a large boiling tube, the mouth of which is plugged with cotton-wool, while through the cotton-wool, and with its bulb in the sand, runs a thermometer.

The tube, arranged as described and containing the sand, is then stood in a beaker of water and the temperature raised to boiling point and kept there for some time. The sand should attain a temperature of 100° C. but this should be checked by means of the thermometer and if a lower temperature only is reached, the exact temperature should be noted.

The tube containing the sand is then rapidly removed from the beaker and the sand tipped instantly into the water in the calorimeter.

The remainder of the experiment and the calculation are carried out as in Expt. 2. (See note *c.*)

4. Find the specific heat of alcohol.

The experiment is carried out as in Expt. 2, but only 50 grs. of water should be placed in the calorimeter while 50 grs. of alcohol are heated to about 40° C. in the beaker and then quickly poured into the water. The temperature of the resulting mixture is found and the calculation made as before. (See note *d.*)

NOTES

Note a. These experiments illustrate the different capacities for heat possessed by different substances.

In the two experiments the same quantity of water is in both cases raised to the same temperature, namely 40° C. In one case this water is poured into 100 grs. of cold water, in the other into 100 grs. of cold alcohol.

It will be found that the temperature of the alcohol will be raised more than the temperature of the cold water. That is, the addition of equal quantities of heat to equal weights of alcohol and water will raise the temperature of the alcohol to a higher point than that of the water. In other words, it takes less heat to raise the temperature of one gramme of alcohol one degree, than it does to raise the temperature of one gramme of water one degree. The heat capacity of alcohol is therefore less than that of water.

Note b. During these experiments, the meaning of "specific heat" should be borne in mind.

The specific heat of any substance can be defined as the number of calories of heat required to raise the temperature of one gramme of the substance one degree Centigrade. The word "calorie" used in this definition can be defined as the amount of heat required to raise one gramme of water one degree Centigrade. It will be seen from this that the term "specific heat" can be given a second definition, namely, the ratio between the amount of heat required to raise a given weight of the substance from one temperature to a higher temperature and the amount of heat required to raise the same weight of water through the same range of temperature. In working out the results in these experiments the fact to be remembered is that the heat lost by the warm body must be equal to the heat gained by the cold body and the calorimeter together. Now in Expt. 2, the heat, expressed in calories, lost by the hot body is

$$SW(100 - T_1),$$

where S = specific heat of the metal,

W = weight of the metal in grammes,

and T_1 = final temperature in the calorimeter.

The heat gained by the cold water in the calorimeter is

$$W_1(T_1 - T),$$

where W_1 = weight of water in the calorimeter,

T_1 = final temperature of the water,

and T = initial temperature of the water.

The heat gained by the calorimeter is

$$S_1 W_2 (T_1 - T),$$

where S_1 = specific heat of the calorimeter metal,

W_2 = weight of calorimeter in grammes,

and T_1 and T have the same meaning as before.

Now (1) must equal (2) + (3).

That is

$$SW (100 - T_1) = W_1 (T_1 - T) + S_1 W_2 (T_1 - T).$$

If S_1, the specific heat of the calorimeter material, is known, all the terms in the above equation are also known with the exception of S and this can be calculated.

Note c. The result is worked out exactly as in Expt. 2, except that, if the sand does not attain a temperature of 100° C., the actual temperature must be introduced in the final equation instead of the term "100° C."

Note d. The result is worked out as in the two previous experiments. The temperature of the alcohol must not be taken above *40° C. or some will be lost by evaporation and there is a* danger of it catching fire whilst being warmed.

XLII

LATENT HEAT

1. Into a small beaker place a quantity of water and about an equal volume of ice broken up into small pieces. Stir with a thermometer and note that the temperature quickly falls to 0° C. At this point stand the small beaker in a larger one containing warm water and continue the stirring vigorously. Read the temperature at regular short intervals and note that as long as any ice remains the temperature of the mixture of ice and water is constant, but directly the ice disappears the temperature begins to rise in a regular manner. (See note *a*.)

2. Find the latent heat of fusion of ice.

Weigh a small calorimeter and into it pour about 80 c.c. of water, and weigh again. Heat the water in the calorimeter over a small bunsen flame until the temperature is about 40° C., and then stand the calorimeter on a cork mat on the bench. Take some lumps of ice and remove as much of the water as possible from their surface by gently pressing them between filter papers. Now read accurately the temperature, T, of the water in the calorimeter and drop in ice in small quantities at a time until the temperature has fallen to about 10° C. Read this temperature, T_1, accurately with a thermometer. The water should be kept well stirred with the thermometer during the melting of the ice, and the stirring must be continued until every bit has disappeared. The calorimeter and its contents are now again weighed, when the increase in weight will give the weight of the ice added. The following facts should now be tabulated:

Weight of calorimeter, weight of water taken, weight of ice added, initial temperature T, final temperature T_1, and the specific heat of the calorimeter material. This last figure will be supplied to you. From these facts calculate the latent heat of fusion of ice. (See note *b*.)

3. Find the latent heat of steam.

You are supplied with a small calorimeter and a flask fitted with a leading tube bent twice at right angles, and, in the downward limb, a small trap is provided to hold back condensed water when steam is being produced from the flask. First weigh the calorimeter empty and then weigh again, when about three-quarters full of cold water. The difference in weight will give the weight of water added. Now stand the calorimeter on a cork mat on the bench.

Having filled the flask provided about one-third full with water, fit to it the leading tube and steam trap and get it boiling vigorously

over the bunsen flame. The trap should keep back any small quantities of condensed water and a jet of dry steam should be issuing from the outlet tube. Take the temperature, T, of the water in the calorimeter and blow steam from the jet into the water contained therein until the temperature has risen to about 40° C. Read this temperature, T_1, accurately with a thermometer which should be used as a stirrer to mix thoroughly the liquid in the calorimeter. Remove the steam jet from the calorimeter and again weigh the latter. The increase in weight will give the weight of steam condensed in the water. Now tabulate the following facts. Weight of calorimeter, weight of water taken, weight of steam condensed, initial temperature, T, final temperature, T_1, and the specific heat of the calorimeter material. The last named figure will be supplied you. From these figures calculate the latent heat of steam. (See note *c*.)

NOTES

Note a. This experiment demonstrates that heat may be absorbed by a substance without any change of temperature. In this case heat is passing continuously from the warm water in the outer beaker to the material in the inner beaker, but, as long as any ice is present, there is no rise in temperature of the material in the inner beaker. The heat is being utilised, not to raise the temperature but to change the state of the material. In this case solid ice into liquid water. Heat utilised in this way is known as latent heat. Another case of latent heat occurs when water is changed into steam, when it can be shown that a large quantity of heat is required to change liquid water at 100° C. into steam at 100° C., that is to change the state of the water without raising the temperature.

Note b. The definition of the latent heat of fusion of ice should be borne in mind in working out the results of this experiment. It can be defined as the number of calories required to convert one gramme of ice at 0° C. into one gramme of water at 0° C. The other essential fact to be remembered is that the heat lost by the water and the calorimeter must equal the heat gained by the ice and the water produced from the ice. Consider first the heat lost by the water originally placed in the calorimeter. This must be represented by

$$W(T - T_1), \qquad \ldots\ldots(1)$$

where W = weight of water in grammes,
T = initial temperature,
T_1 = final temperature.

The heat lost by the calorimeter will be

$$W_1 S(T - T_1), \qquad \ldots\ldots(2)$$

where W_1 = weight of the calorimeter,
S = specific heat of the calorimeter material,
and T and T_1 have the same meaning as before.

Now the heat gained by the ice, and the water produced by the ice, can be considered in two portions, first, the heat required to turn ice at 0° C. into water at 0° C. and, second, the heat required to raise the water at 0° C. to the final temperature T_1. The heat required to change the ice at 0° C. into water at 0° C. will be given by the term

$$W_2 L, \qquad \ldots\ldots(3)$$

where W_2 is the weight of ice added and L the latent heat of fusion. The heat required to raise W_2 grammes of water from 0° C. to the final temperature T_1 will be

$$W_2(T_1 - 0), \text{ that is } W_2 T_1. \qquad \ldots\ldots(4)$$

Now from what has been said (3) + (4) = (1) + (2), that is

$$W_2L + W_2T_1 = W(T - T_1) + W_1S(T - T_1).$$

In this equation all the terms are known except L which can there fore be calculated.

Accurate determinations give the latent heat of ice as 79·25.

Note c. The definition of the latent heat of steam should be borne in mind. The latent heat of steam can be defined as the number of calories required to convert one gramme of water at 100° C. into one gramme of steam at the same temperature. By similar reasoning to that employed in note *b*, the latent heat of steam can be calculated.

Let the following symbols be employed:

W = weight of water placed in the calorimeter,
W_1 = weight of calorimeter,
W_2 = weight of steam condensed,
T = initial temperature,
T_1 = final temperature,
S = specific heat of calorimeter material.

The heat gained by water in the calorimeter is

$$W(T_1 - T). \qquad \text{......(1)}$$

Heat gained by calorimeter is

$$W_1S(T_1 - T). \qquad \text{......(2)}$$

Heat lost when steam condenses to water at 100° C. is

$$W_2L. \qquad \text{......(3)}$$

Heat lost when the water from the steam cools from 100° C. to the final temperature, T_1, is

$$W_2(100 - T_1). \qquad \text{......(4)}$$

Now (3) + (4) = (1) + (2), that is

$$W_2L + W_2(100 - T_1) = W(T_1 - T) + W_1S(T_1 - T).$$

In this equation all terms are known except L which can be calculated. Accurate determinations give the latent heat of steam as 536.

XLIII

SURFACE TENSION AND CAPILLARITY

1. Take two blocks of wood with planed surfaces. Wet one face of the first block with water, leaving a mere film on the surface, and treat a corresponding face of the second block with paraffin oil in a similar manner. On to the surface wetted with water place a single drop of paraffin oil and note that the oil spreads as a thin film over the entire surface. On to the surface wetted with paraffin oil place a single drop of water and note that the drop stands on the surface as a rounded globule and shows no tendency towards spreading evenly as in the case of the oil. (See note *a*.)

2. Remove one pan and its supports from the arm of an open balance. In the place of the pan attach a ground glass plate to the beam of the balance by means of a piece of cotton about three or four inches long, tied at one end to the balance arm and at the other end attached with sealing wax to the central point of the glass plate. Counterpoise the glass plate and cotton by means of weights added to the remaining pan of the balance. Now place under the glass plate a beaker or dish containing water and larger in diameter than the plate.

Raise the beaker until the surface of the water just touches the glass plate when the latter is horizontal. By adding weights to the balance pan measure the force required to pull the glass surface away from the water surface. Calculate the area of the plate and state your result in grammes per square centimetre. (See note *b*.)

3. Repeat Expt. 2 but when the glass plate is lying on the water surface add only half the weight needed to separate the two surfaces to the balance pan. Then add to the surface of the water in the beaker a few drops of ether and note that the plate and water separate instantly. (See note *c*.)

4. Fix up capillary tubes of varying diameter in a beaker containing coloured water and note the different heights to which the water will rise in the tubes, observing that these heights are inversely proportional to the diameter of the tubes. (See note *d*.)

5. Take three tubes about 40 cms. long and 0·5–1 cm. internal diameter and tie over one end of each a piece of fine muslin. Fill the tubes with dry sand, loam and clay respectively, tapping the tubes to ensure regular filling. Clamp the tubes in a vertical position with their covered ends in a beaker full of water and note (*a*) the rate at which the water rises in the three different materials and (*b*) the final level to which the water rises in the three different tubes. (See note *e*.)

6. Fill a burette with water to the zero mark and allow the water to drop slowly from the burette until 10 c.c. have run out. Count the number of drops which go to make up this volume. Repeat the experiment, using alcohol instead of water in the burette. Note the difference in the number of drops required in the two cases to make up equal volumes. (See note *f*.)

7. Take two beakers of large size and provide each with a glass tube passing from the bottom to the top, bending down over the edge of the beaker to the bottom on the outside and then bent round again till it runs vertically to a height a few inches above the top of the beaker. This tube should not be too narrow and should preferably be about 1 cm. internal diameter. The end of the tube inside the beaker should be covered by tying on a fine piece of muslin. Having placed the tubes in position, the beakers should be filled with a fine soil, packed evenly as it is run in. When the beakers are full of soil press down the surface in one with some smooth instrument like a pestle, while in the other mulch the surface to the depth of about an inch. Now add water down the tube until it stands permanently to about the depth of an inch in the beakers. Mark this depth on the beaker. Allow the beakers to stand undisturbed in the laboratory and add water down the tubes from time to time so as to keep the level in the beakers constant. Keep a record of the amount of water added to each beaker, remembering that it corresponds to the amount of water evaporated from the surface of the soil. Note which beaker requires the most water. (See note *g*.)

NOTES

Note a. This experiment illustrates the different surface tensions of the two liquids when in contact with one another. The surface tension of the water is high and gives a skin effect to the drop of water on the oiled surface, pulling the water up into a rounded globule. The oil on the other hand having a low surface tension, has no tendency to be drawn up into a globule and spreads evenly over the water-wetted surface.

Note b. In this experiment the force of "cohesion" between two surfaces is illustrated. A very considerable force is required to separate the glass and water surfaces and this is measured by the weight added to the balance pan to effect the separation.

Note c. The weight required to separate a solid and a liquid surface, as in this experiment, will depend on the liquid used. The weight added to the balance pan is insufficient to separate the glass and water surfaces but when ether, a liquid of low surface tension, is added, the weight is more than sufficient and the surfaces are separated immediately.

Note d. The rise of a liquid in a capillary tube is, for any given liquid under fixed conditions, inversely proportional to the diameter of the tube, that is, if two tubes have diameters represented by 1 and 2, the heights to which the liquids will rise in the tubes will be in the proportion of 2 to 1.

Note e. The rise of water in these tubes takes place in the small interstices between the soil particles, these spaces acting as a collection of capillary tubes. The mean diameter of these tubes will depend on the average size of the soil particles. They are comparatively large where the soil particles are large, as in the case of the sand and small where the soil particles are small, e.g. in the case of the clay. The water in these experiments will finally rise to a greater height therefore in the tube filled with clay than in the tube filled with sand. The rate at which the water rises is an entirely separate question and depends on several factors. It will be noted, for example, that it rises much more quickly in the sand than in the clay.

Note f. The size of a drop coming from any given jet will depend on both the specific gravity and the surface tension of the liquid concerned. The surface tension causes the skin effect already mentioned and tends to hold the drop together, so that, other things being equal, the greater the surface tension the bigger the drops. The specific gravity has also to be considered, since a denser liquid will give a

heavier drop and so cause a greater tendency for the drop to break away from the jet. In this experiment the alcohol, in spite of having a lower specific gravity, breaks away from the jet in smaller drops than the water, owing to its lower surface tension.

Note g. In this experiment the capillary soil tubes are similar in both beakers except near the surface of the soil. In the pressed soil beaker the capillary tubes are complete right up to the surface whereas in the mulched soil beaker the capillary tubes are broken where the mulch begins. In the second case therefore the flow of water upwards in the beaker will be partially stopped where the mulch begins and the evaporation from this beaker will be less than from the beaker with the pressed soil. This different rate of evaporation will be shown by the different amounts of water added to the two beakers to keep the water level constant.

APPENDIX

Table I

Element	Symbol	Atomic Weight	Valency	Oxide(s)	Chloride
Aluminium	Al	27	III	Al_2O_3	Al_2Cl_6
(Ammonium)	NH_4	(18)	I	—	NH_4Cl
Barium	Ba	137	II	BaO	$BaCl_2$
Boron	B	11	III	B_2O_3	BCl_3
Bromine	Br	80	I	—	—
Calcium	Ca	40	II	CaO	$CaCl_2$
Carbon	C	12	IV	CO_2, CO	CCl_4
Chlorine	Cl	35·5	I, VII	—	—
Cobalt	Co	59	II	CoO	$CoCl_2$
Copper	Cu	63	I, II	Cu_2O, CuO	Cu_2Cl_2, $CuCl_2$
Fluorine	F	19	I	—	—
Hydrogen	H	1	I	H_2O	HCl
Iodine	I	127	I	—	—
Iron	Fe	56	II, III	FeO, Fe_2O_3	$FeCl_2$, Fe_2Cl_6
Lead	Pb	206	II	PbO	$PbCl_2$
Magnesium	Mg	24	II	MgO	$MgCl_2$
Mercury	Hg	200	I, II	Hg_2O, HgO	Hg_2Cl_2, $HgCl_2$
Nitrogen	N	14	III, V	N_2O, NO, N_2O_3, NO_2, N_2O_5	NCl_3
Oxygen	O	16	II	—	—
Phosphorus	P	31	III, V	P_2O_3, P_2O_5	PCl_3, PCl_5
Platinum	Pt	194	IV	—	$PtCl_4$
Potassium	K	39	I	K_2O	KCl
Silica	Si	28	IV	SiO_2	$SiCl_4$
Silver	Ag	108	I	Ag_2O	AgCl
Sodium	Na	23	I	Na_2O	NaCl
Sulphur	S	32	II, IV, VI	SO_2, SO_3	—
Zinc	Zn	59	II	ZnO	$ZnCl_2$

Table II

To convert any given weight of the compound whose formula is given in Column I into the equivalent quantity of the compound whose formula is given in Column II, multiply by the factor given in Column III.

I	II	III
$P_2O_5 24MoO_3$	P_2O_5	0·0396
$(NH_4)_6(PO_4)_2 24MoO_3$	P_2O_5	0·038
$Mg_2P_2O_7$	P_2O_5	0·639
K_2PtCl_6	K_2O	0·194
$K_2NaCo(NO_2)_6H_2O$	K_2O	0·193
$KClO_4$	K_2O	0·339
P_2O_5	$Ca_3(PO_4)_2$	2·183
$Ca_3(PO_4)_2$	P_2O_5	0·458

Table III

One cubic centimetre of a normal solution contains:

Acids	*Alkalis*
·049 grs. H_2SO_4	·04 grs. NaOH
·0365 grs. HCl	·053 grs. Na_2CO_3
·063 grs. HNO_3	·017 grs. NH_3
	·056 grs. KOH
	·028 grs. CaO

One c.c. of any normal acid neutralises 1 c.c. of any normal alkali. Deci-normal solutions are one-tenth of the strength given above. Other figures which may be required are:

1 c.c. N/10 Permanganate = ·00316 grs. $K_2Mn_2O_8$ = ·0056 grs. Fe
= ·0008 grs. O
1 c.c. N/10 Silver Nitrate = ·017 grs. $AgNO_3$ = ·00355 grs. Cl

Table IV

Typical analyses of various soils

(Figures are percentages)

	Heavy clay	Medium clay	Loam	Chalky	Sandy	Silty
Fine gravel ...	·50	1·40	1·45	4·60	6·72	·60
Coarse sand ...	9·87	29·03	18·28	25·25	50·93	·60
Fine sand ...	7·80	21·15	45·60	15·44	20·16	35·30
Coarse silt ...	10·60	7·95	14·14	9·14	6·71	19·00
Fine silt	15·57	9·25	7·56	8·50	5·16	14·63
Clay	34·64	16·18	6·61	1·0	1·63	18·00
Residual Moisture	3·14	3·08	1·68	1·63	·86	2·47
Organic Matter ...	10·51	6·62	4·11	11·80	2·70	6·60
$CaCO_3$	5·34	4·34	·11	39·60	·05	·34
Nitrogen	·20	·201	·154	·21	·129	·209
P_2O_5	·097	·134	·074	·274	·09	·16
K_2O	1·30	·592	·29	·232	·242	1·00
Insoluble Residue	60·35	75·40	88·15	47·57	83·70	76·62
Stones	0·60	1·40	2·40	10·00	13·10	0·00

Table V

Typical analyses of various plant ashes

(Figures are percentages)

	Potato	Wheat	Broad Bean	Barley
Potash, K_2O ...	60·37	31·16	42·49	20·15
Soda, Na_2O	2·62	2·25	1·34	2·53
Lime, CaO	2·57	3·34	4·73	2·60
Magnesia, MgO ...	4·69	11·97	7·08	8·62
Ferric Oxide, Fe_2O_3	1·18	1·31	·57	·97
Phosphoric Acid, P_2O_5	17·33	46·98	38·74	34·87
Sulphuric Acid, SO_3	6·49	·37	2·53	1·39
Silica, SiO_2	2·13	2·11	·73	27·64
Chlorine, Cl	3·11	·22	1·57	·93

Table VI

Composition of Manures

Farmyard Manures

		Water	Nitrogen	Phosphoric Acid, P_2O_5	Potash, K_2O
1.	Fresh long straw ...	66·17	0·544	0·318	0·673
2.	No. 1 after rotting ...	75·4	0·597	0·454	0·491
3.	Rothamsted average ...	76·0	0·64	0·23	0·32
4.	Fresh liquid manure ...	98·02	0·044	0·051	0·355
5.	Old ,, ,, ...	99·13	0·026	0·014	0·22

Table VII

Nitrogenous Manures

No.	Manure	Moisture	Nitrogen	Equivalent to Nitrate of Soda	Equivalent to Ammonia	Equivalent to Ammonium Sulphate	Insoluble Impurities
1.	Nitrate of Soda		16·22	98·47			
2.	,,		15·55	94·47			
3.	,,		*15·91*	*96·59*			
4.	,,	2·97	15·24	92·5			
5.	,,	2·62	15·30	92·9			
6.	Ammonium Sulphate	4·24	20·27		24·61	95·57	·07
7.	,,	3·70	20·35		24·71	95·96	·28
8.	,,	3·02	20·44		24·82	96·36	·16
9.	Cyanide		15·65		19·0		
10.	Nitrate of *Lime*		13·0				

Table VIII

Phosphatic Manures

No.	Manure	P_2O_5 %	Equivalent to $Ca_3(PO_4)_2$ rendered soluble	Equivalent to $Ca_3(PO_4)_2$	$CaCO_3$	Free CaO	Passing through 10,000 mesh sieve
1.	Superphosphate	12·72	27·65				
2.	,,	10·29	22·37				
3.	,,	15·90	34·56				
4.	Basic slag	16·56	—	36·00			79·61
5.	,, ,,	19·73		42·90			80·60
6.	,, ,,	14·46		31·44			84·54
7.	Coprolites	32·61		70·90	10·28		
8.	,,	24·84		54·00	10·00		
9.	Mineral phosphate (Liege)	26·00		56·70	6·8		
10.	Mineral phosphate (Carolina)	26·5		57·77	18·2		
11.	Mineral phosphate (Algeria)	30·5		66·49	17·0		
12.	Bone ash	37·72		82·00	4·4		

Table IX

Nitrogenous and Phosphatic Manures

No.	Manure	P_2O_5 %	$Ca_3(PO_4)_2$ (Total)	$Ca_3(PO_4)_2$ soluble	Nitrogen	Equivalent to Nitrogen as Ammonia	Potash K_2O	Water	Loss on Ignition
1.	Guano	15·43	33·64	—	4·40	5·34	—	16·15	28·06
2.	,,	17·54	38·24	—	5·58	6·77	2·5	23·79	—
3.	,,	12·25	26·71	—	11·0	13·16	2·5	25·88	—
4.	,,	13·52	29·47	—	14·37	17·45	2·5	21·25	—
5.	,,	24·27	52·92	—	1·45	1·76	—	—	—
6.	Bone Meal	17·74	38·68	—	4·07	4·94	—	—	—
7.	Dissolved Bones	16·14	35·19	20·8	2·48	3·01	—	—	—
8.	Raw Bone Meal	18·28	39·86	—	4·13	5·01	—	—	—
9.	Steamed Bone Meal	29·07	63·37	—	1·86	2·26	—	—	—
10.	Soot	·23	0·50	—	4·27	5·18	—	69·88	
11.	Rape Dust	1·69	3·69	—	4·97	6·03	1·17	—	—
12.	Hoof Shaving	—	—	—	13·83	16·79	—	—	—
13.	Shoddy	—	—	—	5·12	6·33	—	85·18	
14.	Native Guano	1·28	2·79	—	0·56	0·68	—	—	—

Table X

Potassium Manures

No.	Manure	Potassium Sulphate	Potassium Chloride	Equivalent to Potash K_2O	Magnesium Sulphate	Sodium Chloride	Water
1.	Kainit ...	—	20·5	12·12	15·9	46·8	12·8
2.	Sulphate of Potash, 96 %	97·2	0·30	52·67	0·7	0·2	0·7
3.	Muriate of Potash, 85 %	—	83·50	49·37	0·4	14·50	1·1

Table XI

Tension of aqueous vapour in millimetres of mercury

6° C.	7·00	20° C.	17·39
7	7·49	21	18·50
8	8·02	22	19·66
9	8·57	23	20·89
10	9·17	24	22·18
11	9·79	25	23·55
12	10·46	30	31·55
13	11·16	40	54·91
14	11·91	50	91·98
15	12·70	60	148·79
16	13·54	70	233·08
17	14·42	80	354·62
18	15·36	90	525·39
19	16·35	100	760·00

Table XII

Conversion Tables

(a)	1 inch = 0·0254 metre	1 millimetre = 0·03937 inch
	1 foot = 0·3048 ,,	1 metre = 39·3701 inches
	1 yard = 0·9144 ,,	1 ,, = 3·2809 feet
	1 mile = 1·6093 kilometres	1 ,, = 1·0936 yards
		1 kilometre = 0·6214 mile
(b)	1 sq. yard = 0·8361 sq. metre	1 sq. metre = 1·196 sq. yards
	1 acre = 4046·7 sq metres	1 hectare = 2·471 acres
	1 sq. mile = 2·59 sq. kilometres	1 sq. kilometre = 0·3861 sq. mile
(c)	1 pint = 568·23 c.c.	1 litre = 61·036 cubic inches
	1 gallon = 4·546 litres	1 ,, = 1·76 pints
	1 cu. foot = 28·31 litres	1 ,, = 0·22 gallon
	1 cu. yard = 764·4 litres	1 stere = 1·308 cubic yards
(d)	1 gramme = 0·0648 gramme	1 gramme = 15·432 grains
	1 ounce = 28·35 grammes	1 kilogramme = 2·2046 lbs.
	1 lb. = 453·59 ,,	1 tonne = 0·984 ton
	1 ton = 1016·05 kilogrammes	

Table XIII

Miscellaneous Data

Weight of soil to a depth of 9 inches over 1 acre	=	3,000,000 lbs.
Average weight of air over 1 sq. inch of surface (pressure)	=	15 ,,
Weight of 1 gallon water	=	10 ,,
Weight of 1 cubic foot water	=	62·4 ,,
Weight of 1 cubic foot average arable soil (dry)	=	84·5 ,,
Weight of 1 bushel wheat	=	63 ,,
Weight of 1 bushel barley	=	56 ,,
Weight of 1 cubic yard of hay	=	72 ,,

Table XIV

Solubilities of some of the common salts and oxides

	K	Na	NH_4	Mg	Ca	Ba	Ferrous iron	Ferric iron	Ag	Al	Cu
Phosphates	*a*	*a*	*a*	*i*	*i*	*i*	*i*	*i*	*i*	*i*	*i*
Chlorides	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*q*	*a*	*a*
Hypochlorites	all the hypochlorites are soluble in water										
Chlorates	,, chlorates ,, ,, ,,										
Sulphides	*a*	*a*	*a*	*a*	*a*	*a*	*i*	*i*	*i*	*i*	*i*
Sulphites	*a*	*a*	*a*	*a*	*i*	*i*	*i*	*i*	*i*	*i*	*i*
Sulphates	*a*	*a*	*a*	*a*	*s*	*q*	*a*	*a*	*s*	*a*	*a*
Iodides	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*q*	*a*	*a*
Carbonates	*a*	*a*	*a*	*i*	*i*	*s*	*i*	*i*	*i*	*i*	*i*
Silicates	*a*	*a*	*i*	*i*	*i*	*i*	*i*	*i*	*i*	*i*	*i*
Nitrites	all the nitrites are soluble in water										
Nitrates	,, nitrates ,, ,, ,,										
Ferro-cyanides	*a*	*a*	*a*	*a*	*a*	*s*	*d*	*d*	*q*	–	*q*
Ferri-cyanides	*a*	*a*	*a*	*a*	*a*	–	*d*	*a*	*q*	–	–
Cyanides	*a*	*a*	*a*	*a*	*a*	*s*	*d*	–	*q*	–	*d*
Acetates	all the acetates are soluble in water										
Oxalates	*a*	*a*	*a*	*s*	*s*	*s*	*s*	*s*	*s*	*s*	*s*
Oxides	*a*	*a*	–	*i*	*s*	*a*	*i*	*i*	*i*	*i*	*i*

a = soluble in water
s = slightly soluble in water, but soluble in dilute acids
i = insoluble in water, but soluble in acids
d = insoluble in water, soluble with difficulty in acids
q = insoluble in water or acids

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